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DEVELOPMENT OF METHOD FOR CARCINOGENIC VAPOR ANALYSIS IN AMBIENT ATMOSPHERES

Edo E. Pellizzari

Research Triangle Institute

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by

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ABSTRACT

Analytical techniques and instrumentation were developed and evaluated for the collection and analysis of carcinogenic and mutagenic vapors occurring in ambient air. The areas of investigation included (a) the design and testing of a cartridge sampler for concentrating trace quantities (ng/m^3) of hazardous substances from air, (b) the design, fabrication and evaluation of a thermal desorption inlet-manifold for recovering vapors trapped on an analyte and sample transfer into an analytical system, (c) the evaluation of thermal desorption as a technique for recovering hazardous vapors from sorbents, (d) the development and performance of a field sampling system for collecting trace quantities of vapors, and (e) the application of techniques and instrumentation developed under this program to the analysis of hazardous vapors in ambient air.

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SECTION I

CONCLUSIONS

An analytical technique was developed for evaluating collection efficiencies of candidate sorbents during the concentration of hazardous vapors from a flowing stream. The polymeric beads - Tenax GC, Porapak Q, Chromosorb 101 and 104 - were $\geq$ 90% efficient in trapping hazardous vapors such as epoxides, β-lactones, sulfonates, sultones, N-nitrosamines, chloroalkyl ethers, aldehydes and nitro compounds from synthetic air/vapor mixtures at 0.25 l/min. Tenax GC and Chromosorb 101 were also tested at sampling rates up to 9 l/min and efficiencies of $\geq$ 90% were maintained. Carbowax 400 and 600 and oxypropionitrile coated or chemically bonded to supports and activated carbons were also highly efficient.

A thermal desorption inlet-manifold for recovering and transferring hazardous substances from sorbents to a gas-liquid chromatograph or a gas-liquid chromatograph-mass spectrometer was developed. The interface consisted of a desorption chamber, a six-port two position high temperature low volume valve, a Ni capillary trap and a temperature controller. This unit was utilized to determine the temperature rise times in the center of cartridge samplers for a variety of sorbents under isothermal chamber temperatures. The heating rates were: PCB and BPL activated carbons > oxypropionitrile and carbowax 400 chemically bonded to Poracil C > Chromosorb 104 > Tenax GC > Chromosorb 101. The heating rates were linear for all sorbents up to 65% of the set desorption chamber (60-90 sec) but required several minutes thereafter to reach the final temperature. Since the percent recovery of several hazardous vapors adsorbed on Tenax GC using this inlet-manifold was $\geq$ 90% at the 50 ng level, it was concluded that the designed system was satisfactory for analysis of cartridge samplers.

Design criteria were developed for a field sampling system for collecting pollutants using a cartridge containing a solid sorbent. The relationship between the ambient vapor concentration, the total volume of air required and the time required for sampling at various flow rates were important considerations in the design specifications. It was concluded that the power required to pump air through sorbent packed tubes was a function of pressure differential (ΔP) across the tube under flow conditions. The ΔP was found to be related to (1) sampling rate, (2) diameter and length of cartridge, (3) particle size distribution, and (4) particle shape. Based upon ΔP the power requirements for a pumping system was calculated and applied to the fabrication of a field sampler.

The methodology and instrumentation developed under this program was also applied to the analysis of air samples from the Los Angeles Basin area. Using glc-ms-comp techniques, many aliphatic and aromatic compounds were identified in these preliminary studies. The relative intensities of single ion plots for ions representing aliphatic and aromatic cracking patterns revealed that Tenax GC did not efficiently trap background aliphatic constituents; a desirable feature since most hazardous vapor of interest are semipolar/polar compounds. It was concluded that improved techniques for resolving background pollutants occurring at high concentrations from trace hazardous vapors need to be developed.

One oxygenated compound of significant interest tentatively identified as styrene oxide was discovered in air from West Covina and Santa Monica, CA.

SECTION II

RECOMMENDATIONS

Four major phases of research in the current program are recommended to be expanded and pursued. These are listed as follows:

(1) Sampling -

A concerted effort should be undertaken to collect field samples at geographical sites postulated to contain hazardous (mutagens, carcinogens and other alkylating agents) compounds under study. The effects of transportation and storage on adsorbents and reliability and accuracy of analysis for collected pollutants, and potential sources of contamination should be determined. Experimental criteria required for optimum performance of adsorbents should be established. It is recommended that an alternate backup sampling device also be examined. The sampling devices should be improved and the system miniaturized for portability.

(2) Inlet-manifold unit -

The strengths and weaknesses undercovered in this report should be considered for perfection of the design of the thermal desorption unit; it should interface efficiently with a glc and glc-ms.

(3) Resolution of pollutant mixture -

Techniques for the separation of hazardous substances under study from the many hundreds of organic pollutants which are of secondary interest at this stage should be developed and perfected. It is recommended that the identity and relative quantities of background organic pollutants which interfere with the major goals be established.

(4) Characterization of hazardous compounds -

The unequivocal characterization of atmospheric pollutants of interest and those hazardous to living organisms is recommended using methodology and instrumentation developed under this research program. Finally, the specifications for routine assay of hazardous substances based on the discovered ones should be delineated.

SECTION III

INTRODUCTION AND BACKGROUND

CARCINOGENIC VAPORS IN AMBIENT ATMOSPHERE

Carcinogenic vapors have been postulated to occur in the atmosphere,[1-3] however until the present program was initiated no serious and thorough endeavor had been made to collect and determine these substances. Epoxides, peroxides, aldehydes, ketones, lactones, sulfonates, sultones, and nitroso and nitro compounds have been isolated in laboratory experiments during olefin oxidation, ozonization, sulfonation, nitrosation and nitration[4]. Some of these compounds and reaction mixtures have demonstrated carcinogenic activity in animals[5-10]. For example, the exposure of mice (strain A or C57B) to an atmosphere containing ozonized gasoline increased the incidence of tumors[6].

Because unsaturated hydrocarbons constitute a large fraction of organic air pollutants, it is reasonable to anticipate that their oxidation products and their production of reaction with NO_x and SO_x, whether spontaneously or photochemically induced, may also be present in ambient atmosphere[1]. Many types of alkylating and arylating agents are being introduced directly at a continually increasing rate into our environment, e.g. as industrial intermediates in organic synthesis, organic solvents for various chemical processes, as cross-linking agents in manufacturing processes, as medicines, and as antibacterial and fungistatic agents.

There is a strong indication that nitrosamines are present in the atmosphere; their identification in cigarette smoke has been confirmed[1]. Alkylating compounds resulting from limited-aeration smouldering of plastics, paper, and cellulose as well as auto-exhaust gases have been demonstrated to occur and have been postulated as a health hazard in industrial areas[2].

On the basis of the current knowledge of air pollution, most of the potentially deleterious vapors which could be formed in or expelled into the atmosphere could be therefore classified as epoxides, β-lactones, peroxides, hydroperoxides, sulfonates, sultones, nitrosamines and α-chloroalkyl ethers. Some of these pollutants may have a short lifetime in the atmosphere.

The National Academy of Sciences panel in a study of the biological effects of atmospheric pollutants has concluded and recommended in their report on Particulate Polycylic Organic Matter[6] "Research is needed on the chemistry and biological activity of air pollutant cocarcinogens and tumor-promoting agents, such as polyphenols and paraffin hydrocarbons, and on the oxidation products of airborne olefins and aromatic hydrocarbons, including the nature of the epoxides, hydroperoxides, peroxides, and lactones formed and their biological properties". Recently, Van Duuren[7-11] summarized a review on the biological properties of carcinogenic vapors with the statement "in view of the obvious importance of these aliphatic compounds (epoxides, hydroperoxides and peroxides), it is imperative that studies be undertaken on the analysis of volatile organic air pollutants". Once the identity of the physiologically active vapors present in polluted atmospheres are known, then investigators can ascertain which substances need to be routinely analyzed, studied epidemiologically and eventually controlled.

The primary mission of this research program has been to develop methodology for the reliable and accurate collection and analysis of mutagenic and carcinogenic vapors present in the atmosphere down to nanogram per cubic meter amounts.

METHODS FOR COLLECTION AND ANALYZING POLLUTANTS FROM AMBIENT AIR

Collection Techniques

The characterization and measurement of extremely minute amounts (ppb) of these hazardous compounds in ambient air has been seriously hampered by the lack of a reliable sampling system and sensitive instrumentation for direct analysis. Special systems have been developed for concentrating trace organic vapors from large volumes of atmosphere and transferring the collected vapors to an analytical system[12-28].

Many collection devices and analytes have been employed by investigators in air pollution. In general, the concentrating techniques have utilized cryogenic[22-27], absorptive[17,28,31] or adsorptive[13-16,18-27] trapping methods. Cryogenic (freeze-out) methods are particularly suitable for analysis of highly volatile substances; however, if liquid nitrogen, oxygen, or solid carbon dioxide/acetone is used as a coolant large quantities of water may accumulate, which is a major problem during chromatographic analysis. Aerosol formation may be also experienced with this technique reducing the trapping efficiency. Drying the gas by passing the air over desiccants prior to cryogenic trapping is not feasible since some solutes may also be scrubbed[29-31]. Nevertheless, the major advantage of this approach is that it is the only technique which permits the collection of low molecular weight air pollutants. Also, oxidation or polymerization of constituents is minimized during their concentration.

Activated carbons (including activated carbon molecular sieves[21]) have been shown to adsorb all of the classes of carcinogenic-type compounds to be studied under this program[13,14,32-34]. Where the adsorption is purely physical, the compounds may be retained and subsequently released without being decomposed. Brooman used activated carbon to adsorb acrolein quantitatively up to the point of breakthrough, then used solvent extraction to recover the trapped substance[14]. Saunders used adsorbent carbon to identify 23 volatile compounds in closed environmental atmospheres[35]. Ethylene oxide has been successively recovered from activated carbon at 30°C; acetaldehyde required 175°[35].

The high surface activity of activated carbons also can produce artifacts during recovery. Formaldehyde decomposes, while methyl ethyl ketone tends to form diacetyl compounds and acetic acid, on activated carbon[35]. Epoxides and peroxides are usually destroyed, hence, activated carbon alone has very limited potential as a sorbent for collecting highly polar and reactive compounds.

Compounds that are sensitive to polymerization or decomposition on activated carbon are generally more so on molecular sieves[20]. For this reason the potential role of molecular sieves is probably limited to removing and recovering simple molecules (H_2O, NH_3, CH_4) from air.

One unique approach which is based on gas and liquid chromatographic principles employs liquid phases uniformly coated on solid supports (e.g. silica, diatomaceous earth, polystyrenes) and these polymers exhibit solution formation with trace organic vapors at ambient temperatures. Williams has reported a collection device for organic compounds such as hexane, benzene, toluene, aldehydes, ketones, and chlorinated hydrocarbons at the part per hundred million level[17]. The device consisted of a tube packed with Chromosorb P coated with the stationary phase, di-n-butylphthalate. During air sampling the collection tube was cooled in dry ice and water was removed by using a drying agent prior to drawing the air through the sampler.

Application of chemically bonded stationary phases[12,28,36,37] to sampling of air pollutants appears to be potentially promising because selectivity can be incorporated by matching the physico-chemical properties of the phase with the pollutants of interest. Because the column packings (glc and lc) are essentially nonextractable, thermally and hydrolytically stable, they exhibit lower backgrounds during thermal desorption than the conventional support coated liquid phases. Permaphase® (E. I. duPont de Nemours & Co.) is formed by reacting silane reagents with the surface of the porous shell of Zipax® and then polymerizing the reagents to yield the desired silicone coating[37]. Ether bonded polymeric coatings are prepared with a variety of functional groups, ranging from very polar to nonpolar, providing a wide range of selectivities (Table 1). The physical characteristics of the stationary phase, such as concentration, film thickness, and structure (i.e. linear or crosslinked), is controlled to obtain the desired properties for affinity to specific classes of trace organics.

By bonding the functional moiety chemically to the core material the vapor pressure is reduced to near zero, hence a low bleed rate is observed. This feature makes these solvents attractive during thermal desorption of trapped organics since a minimal background interference from the polymer-solid support occurs.

Thermal degradation of the bonded functional moiety can result if excessive temperatures are employed. Table I depicts some representative commercially available materials and their physical properties.

Aue has employed a bonded silicone polymer (octadecyltrichlorosilane) to collect several organic compounds from fast-flowing gas streams[12]. Silicone coatings have been shown to concentrate and release many chemical classes of interest to this program; however, lactones, epoxides, and peroxides had not been examined for quantitative analysis.

Table 1. COMMERCIALLY AVAILABLE MATERIALS WITH CHEMICALLY BONDED LIQUID PHASES

Type	Particle Size (mesh)	Polarity[a]	Temperature limit °C
OPN/Porasil C	80/100	M	135
Carbowax 400/Porasil C	100/120	N	150
n-Octane/Porasil C	120/150	P	160
Carbowax 400/Porasil S	80/100	N	200
Phenyl isocyanate/Porasil C	80/100	P	60
Carbowax 4000/Porasil S	80/100	P	200

[a] M = medium, N = nonpolar, P - polar

Other types of bonded functional groups are the "brush"-like stationary phases. These materials are prepared by esterification of the alcoholic groups on silica surfaces. One certain disadvantage of esters is their suspectibility to hydrolysis. Conceivably this might be a problem during collection of trace organics from large volumes of polluted air, if water vapor is also trapped during the solution process. An example of a "Brush" type is polyethylene glycol 400 on silica.

Similarly to the Permaphases® (or Durapak, Waters Assoc.), Poragel-P packings are marketed. These are polystyrene resins with permanently attached functional groups. The surface affinity of the polymer and bonded functional group also allows interaction and thus trapping of organic solutes.

Several polystyrene type polymers are commercially available (e.g. Chromosorb 101, 102, 104) which are used in gas-solid chromatography. Chromosorb 101, a styrene-divinylbenzene polymer adsorbs hydrocarbons, alcohols, acids, esters, aldehydes, ketones, ethers, and glycols. A polar surface is provided by Chromosorb 104 which is an acrylonitrile-divinylbenzene resin. The potential utility of these polymers has not been completely exploited for trace organic vapor analysis.

Leggett, et al.[38] developed a collection cartridge containing 2 g of Porapak Q-S sorbent for concentrating and determining trace organic vapors at ppb levels. Samples were successfully collected at 100 to 1,000 ml/min.

In 1966 Hollis[19] reported the use of porous polyaromatic beads concentrating air samples on a chromatographic column at room temperature. The components were subsequently eluted by temperature programming. With these beads, water is not a major interferent since it is eluted as an early peak without tailing. Hollis successfully adsorbed and desorbed epoxides from these polymer beads. The use of polyalkyl styrene polymers to remove organic vapors from a gas stream was patented in 1972 by Haigh[39].

Dravnicks[40], Crittenden[41], and Jones[3] have described collection systems using Chromosorb 102. All employ thermal desorption for recovering trapped vapors. Jones[3] used this solid sorbent to demonstrate the presence of trace quantities of ethylene sulfite a suspected carcinogen in secular atmospheres.

More recently Bertsch et al.[20] described the collection of trace quantities of organic volatiles from air using Tenax GC a porous polymer of 2,4-diphenyl paraphenylene oxide with a high temperature stability. The trapped substances were subsequently heat desorbed and the mixture resolved by high resolution Ni capillary columns. Several hundred hydrocarbons were recognized and the identity of about 100 was established.

Recovery and Analysis

Because of the limited sensitivity of currently available detectors hazardous substances need to be concentrated from highly dilute samples. A step toward the solution of this problem can be achieved when cartridges containing an appropriate sorbent is used and large volumes of air are forced or drawn through the sampling device whereupon the pollutants are trapped.

Even when the cartridge technique is used, only trace quantities of hazardous pollutants can be expected to accumulate; thus it is imperative that the entire sample be submitted for analysis. Recovery of trapped vapors has been accomplished using thermal[16-21,28] and vacuum[45-47] desorption which allows for direct introduction of the total sample into an analytical system (glc, glc-ms) in the absence of a solvent as a carrier. These methods are subject to artifactual processes such as pyrolysis, polymerization or incomplete recovery. Steam desorption[48,49] and solvent extraction[50-52] of the sorbent alleviate the above mentioned problems; however, volatile pollutants cannot be quantitatively concentrated from dilute solutions and since gas chromatographic (gc) analysis is limited to small aliquots of liquid samples only a fraction of the sample can be examined. As a result the sensitivity of the overall method is greatly reduced.

SECTION IV

PROGRAM OBJECTIVES AND RATIONALE

PURPOSE OF PROGRAM

The general scope of this research program was to develop methodology for reliable and accurate collection and analysis of mutagenic and carcinogenic vapors (collectively referred to hereafter as hazardous compounds) present in trace quantities in the atmosphere down to ng/m^3 amounts. Once the physiologically active vapors present in polluted atmospheres have been determined, investigators can then ascertain what substances need to be routinely analyzed, studied epidemiologically and eventually controlled. The major objectives were:

(1) to determine, develop and fabricate a sampling device for the collection of atmospheric vapors at ambient temperatures, i.e. substances which are volatile solids or liquids in bulk at room temperature and pressure.

(2) to interface the sampling device to an analytical system(s) such as a gas chromatograph or gas chromatograph - mass spectrometer - computer for the characterization and assay of vapors such as N-nitrosamines, sulfones, sultones, sulfonates, epoxides, lactones, anhydrides, aromatic amines, peroxides, hydroperoxides or any other alkylating agents present in polluted atmospheres.

(3) to acquire performance data for the collection and analysis methodology embodying the sampling and interfacing devices. This was to include collection efficiency, reliability of collection and analysis as they relate to environmental factors such as sampling locations, temperature, possible interferences from

other gaseous pollutants, dust load and winds. Artifacts and interferences were to be determined and an effort made to correct or minimize them.

(4) to provide experimental support on -

  a. the efficiency of pollutant collection and bleeding, and their relationship to atmospheric variables,

  b. the effect, if any, of other gaseous pollutants on the reliability of the overall analysis methodology,

  c. the qualitative composition of the ambient vapor sample including those constituents which are of secondary importance or interferences,

  d. the characterization of those pollutants containing functional groups common to hazardous compounds (including alkylating agents)

and e. the estimation of the amounts of some of the atmospheric vapors and especially those containing the functional groups of interest.

GENERAL APPROACH TO PROBLEM

Although the classes of compounds which are to be studied in ambient air under this program cover a wide range of chemical functionalities and physical properties they can be classified as semipolar and polar. For this reason, the reported techniques for collecting and analyzing atmospheric pollutants need to be examined carefully prior to their acceptance as valid methods for use in this program since the literature methods were originally designed for aliphatic and aromatic pollutants occurring at the parts-per-million level.

The experimental approach adoped here was to thoroughly examine and evaluate previously reported methods and provide appropriate modifications which would permit the analysis of hazardous vapors for this program. In doing so, an in depth study beyond the superficial treatment provided in the literature was to be conducted.

Because the concentrations of hazardous vapors sought were anticipated to be in ng/m^3 amounts or less, it was recognized that the major problems would arise with the development of an adequate collection system for concentrating sufficient quantities of material. The relationship between the sampling parameters for collection, say 30 ng of a pollutant, from ambient air is shown in Table 2. It was readily apparent that the sampling time required was directly proportional to the volume of air which must be concentrated for analysis and inversely to the sampling rate at a given pollutant concentration. High sampling rates would be required in order to

Table 2. SAMPLING PARAMETERS FOR COLLECTING 30 NG OF VAPOR FROM AIR

Quantity of Vapor in Air ng/m^3	Volume Required m^3	Sampling Time (hr) at Various Flows (l/min)						
		0.25	1	4	9	20	30	62.5
1	30	2000	500	125	56	25	16.7	8
5	6	400	100	25	11.1	5	3.33	4
10	3	200	50	12.5	5.6	2.5	1.6	0.8
50	0.6	40	10	2.50	1.12	0.5	0.33	0.16
100	0.3	20	5	1.25	0.56	0.25	0.17	0.08
1000	0.03	2	0.5	0.125	0.056	0.025	0.017	0.008

collect enough of a compound within a feasible period of time. For example, a pollutant at a concentration of 1 ng/m^3 would require a sampling volume of a minimum of 30 m^3; at a 1 l/min (a rate most commonly reported by investigators) a sampling time of 500 hr would be needed. Obviously, this would be too long. Sampling rates of 20 l/min or greater would be more satisfactory.

Many factors come into play when high flow rates are employed, particularly the pressure differential developed across the sampling device and subsequently the power requirements needed to achieve the desired rates. Such factors were considered in the development of a collection and sampling system.

During the consideration of a collecting system, specific criteria emerged as important in its design. These were: (1) simplicity, (2) durability, (3) reliability, (4) ability to store samples for two or more weeks, (5) convenience during its transportation to and from sampling site, (6) convenience of its operation and maintaining the collection system during field trails, and (7) readily interfaced with an analytical system. The general concept chosen was a cartridge sampler where the analyte consisted of a solid material capable of trapping vapors of interest.

Since one of the major objectives of this program was to characterize the collected pollutants and because they were suspected to occur in trace amounts, the analytical instrumentation of choice which offered the most promise for achieving these goals were gas chromatography and combined gas chromatography-mass spectrometry. Interfacing the collection cartridge to a gas phase analytical system was believed to best be served by using an interface which would thermally desorb the vapors from the analyte and introduce the entire sample for analysis.

Reagent hazardous vapors listed in Table 3 were chosen to assist in the evaluation of the developed methodology and instrumentation. A compilation of mass spectra has been assembled in the Appendix of this report (Fig. 46-63) for many of these compounds. Additional spectra will be added to establish a library of hazardous vapors for future references purposes.

This report presents the results obtained during the execution of the described experimental plan.

Table 3. REAGENT VAPORS FOR EVALUATING SAMPLING MEDIUM

Chemical Class	Substance
Chloroalkyl ethers	Bis-(chloromethyl)ether alpha-dichloroethyl ether
Lactones	β-propiolactone β-butyrolactone vinylene carbonate parasorbic acid
Nitro and Nitroso	diethyl nitrosamine nitromethane
Sulfones	trional diethyl sulfone
Sulfonates	ethyl methanesulfonate
Epoxides	glycidaldehyde propylene oxide styrene oxide 1,2,3,4-diepoxybutane
Peroxides	methyl ethyl ketone peroxide lauroyl peroxide
Aldehydes and Ketones	glycidaldehyde acrolein methyl ethyl ketone phenylvinyl ketone
Hydroperoxides	cyclohexene hydroperoxide
Acid Anhydrides	maleic anhydride succinic anhydride
Sultones	propane sultone
Sulfolane	tetramethylene sulfone
Aromatic Amines	Aniline
Imino Heterocyclic	Aziridine

SECTION V

DESIGN OF A CARTRIDGE SAMPLER FOR CARCINOGENIC VAPORS

The development of a cartridge containing solid material for the collection and analysis of carcinogenic vapors from ambient atmosphere required a study of the physico-chemical properties of several sorbents. These investigations included (1) the examination of collection efficiencies of several sorbents, (2) the relationship between cartridge dimensions (length and diameter), sorbent particle size, sampling rate and pressure differential, and (3) an estimation of the breakthrough volume for hazardous vapors. During the evaluation of candidate sorbent media, their collection efficiencies and recovery for analysis were independently determined. This was important because a sorbent may have good trapping characteristics but exhibit undesirable effects when a certain type of recovery method was used. The converse was also the case. We therefore designed our experiments to allow an independent assessment of each step.

DETERMINATION OF COLLECTION EFFICIENCIES FOR SEVERAL SORBENTS

The performance of many sorbents as to their ability to extract and retain hazardous vapors from a moving air stream has not been adequately studied. The parameters which are involved in determining the performance of sorbents (collection efficiencies) can be divided into two categories. There are those on the one hand which are related to sampling environment such as flow rate, air temperature, and humidity, and those which are related to the physico-chemical properties of the sorbent such as surface area, particle size and porosity, solute capacity, sorption mechanism, degree of solute affinity, etc. Furthermore, some of these factors which influence sorbent performance are not independent of each other.

Because the collection and analysis of volatile hazardous substances in ng/m^3 amounts from ambient atmosphere requires the selection of a sorbent which is efficient under a variety of sampling conditions, an instrumental technique was designed for evaluating the collection efficiencies of sorbents. This section presents the performance of a number of candidate solid materials for the concentration of substances such as epoxides, β-lactones, sulfonates, sultones, nitrosamines, chloroalkyl ethers, aldehydes, and nitro compounds from an air stream comparable to field sampling conditions.

Experimental

Tenax-GC (60/80 mesh), Chromosorb 101 (100/120), Chromosorb 104 (100/120) and Chromosorb W-HP (100/120) were purchased from Applied Science, State College, Pa. A series of stationary phases chemically bonded to supports including carbowax 400/Poracil C (100/120), oxopropionitrile/Poracil C (80/100), and phenylisocyanate/Poracil C (80/100) were also obtained from Applied Science. Stationary phases consisting of carbowax 600, didecyl phthalate, and tricresyl phosphate and the sorbent Porapak Q were from Supelco, Inc., Bellefonte, Pa.

Carbon derived from coke (PCB and BPL, 12/30) was acquired from Pittsburgh Activated Carbon Division of Calgon Corp., Pittsburgh, Pa. Cocoanut derived carbons (SAL19190 and 580-26) were purchased from Barneby Cheney, Columbus, Ohio.

Ethyl methanesulfonate, β-propiolactone, N-nitrosodiethylamine, 1,2-dichloroethyl ethyl ether, nitromethane, methyl ethyl ketone, and aniline were from Fisher Chemicals, Pittsburgh, Pa. Glycidaldehyde and sulfolane were obtained from Aldrich Chemicals, Milwaukee, Wis. From Eastman Organic Chemicals, Rochester, N. Y. 1,3 propane sultone, maleic anhydride, butadiene diepoxide and propylene oxide were purchased. Styrene epoxide, bis-(chloromethyl)ether and bis-(2-chloroethyl)ether were from K&K Labs., Plainview, N. Y.

The monitoring system shown in Figure 1 was designed and assembled for measuring collection efficiencies. Air (breathing quality, Linde Div. Union Carbide, East Brunswick, N. J.) from a pressurized resorvoir was passed through a scrubbing tower (5 cm i.d. x 30 cm) which contained layers of $CaCl_2$ dessicant and BPL activated carbon (12 x 30 mesh, Calgon Corp., Pittsburgh, Pa.) to remove trace contaminants. Purified air entered the monitoring system at point A as shown in the schematic where the flow rate was controlled with a Sho-Rate 250 flow meter (Model 1357-12F1BAA Brooks Instruments Div., Emerson Electric Co., Hatfield, Pa.) equipped with a teflon diaphragm regulator for compensating downstream pressure changes. The air stream passed through a 2 l cylindrical chamber (point B) fitted with an injection port where known quantities of organic vapors were introduced. The chamber delivered synthetic air/vapor mixtures to the cartridge sampler which contained the sorbent under study (point C) according to the following relationship:

$$C = C_o e^{-Ft/v} \qquad (1)$$

where C_o = initial concentration in chamber

C = concentration in chamber after time, t, has elapsed

F = purging rate (ml/min or l/hr)

V = volume of chamber

The effluent stream from the sampler was split and a flow of 50-100 ml/min was directed to a flame ionization detector (Model 1200, Varian Instruments, Corp., Walnut Creek, Ca.). Because hazardous organic vapors were used in this study, the apparatus between points A and D was contained in a glove box

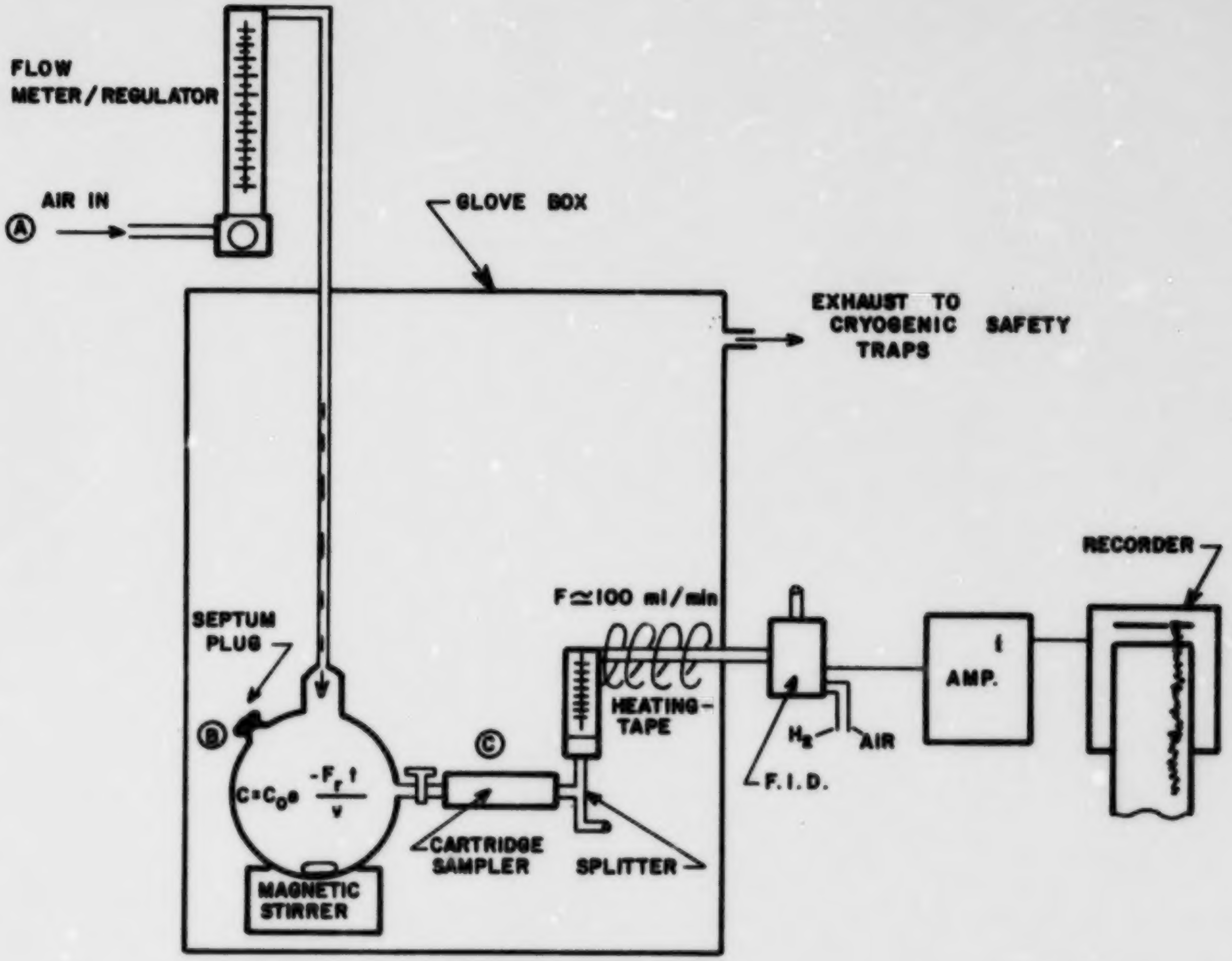

FLOW
METER/REGULATOR
Ⓐ AIR IN
GLOVE BOX
EXHAUST TO CRYOGENIC SAFETY TRAPS
SEPTUM PLUG
Ⓑ
$C=C_0 e^{-\frac{F_r t}{v}}$
MAGNETIC STIRRER
Ⓒ
CARTRIDGE SAMPLER
SPLITTER
$F \simeq 100$ ml/min
HEATING-TAPE
H_2
AIR
F.I.D.
AMP.
i
RECORDER

Figure 1. Monitoring system for hazardous vapors in cartridge effluents

(Kewaunee Scientific Equipment, Adrian, Mich.) which was evacuated by vacuum through cryogenic safety traps. Hydrogen and air flow to the detector were 35 and 250 ml/min, respectively. The detector output signal was amplified (Varian Model 520) and recorded with an Omniscribe® strip chart recorder (Houston Instruments, Houston, Tx.). This apparatus monitored total organic vapor in the cartridge sampler effluent.

Sorbents were packed in glass tubes (1.056 cm i.d. x 10 cm in length) using 1 cm of silanized glass wool plugs for support. The cartridge samplers were inserted in canisters which were constructed from tube L 3/4 in copper fitted with 3/8 in Swagelock® unions. The entrance and exit lines at point C in the monitoring system were 3/8 in o.d. Teflon® (Comco Plastics Corp., Raleigh, N. C.).

To synthesize known concentrations of air/solute vapors mixtures (Table 4), microliter quantities of each organic compound were added to a 2 l cylinderical flask. The flask was heated to 50° and the air/vapor mixture was continuously stirred. An aliquot from this stock resorvoir was transferred to the chamber (point B) in the monitoring system. By continuously monitoring the cartridge sampler effluent with . flame ionization detector the collection efficiency of each sorbent was determined. A decay curve (Fig. 2A) which represented the concentration of the air/vapor mixture leaving the chamber per unit time was established for each mixture and at each purging rate by using empty cartridge samplers. The per cent collection efficiency was estimated by comparing the areas under curves obtained for samplers with and without sorbent (Fig. 2A and 2B).

Results and Discussion

At a sampling rate of 0.25 l/min, over 90% of the synthetic air/vapor mixture is purged through the cartridge sampler in less than 20 min (Table 5).

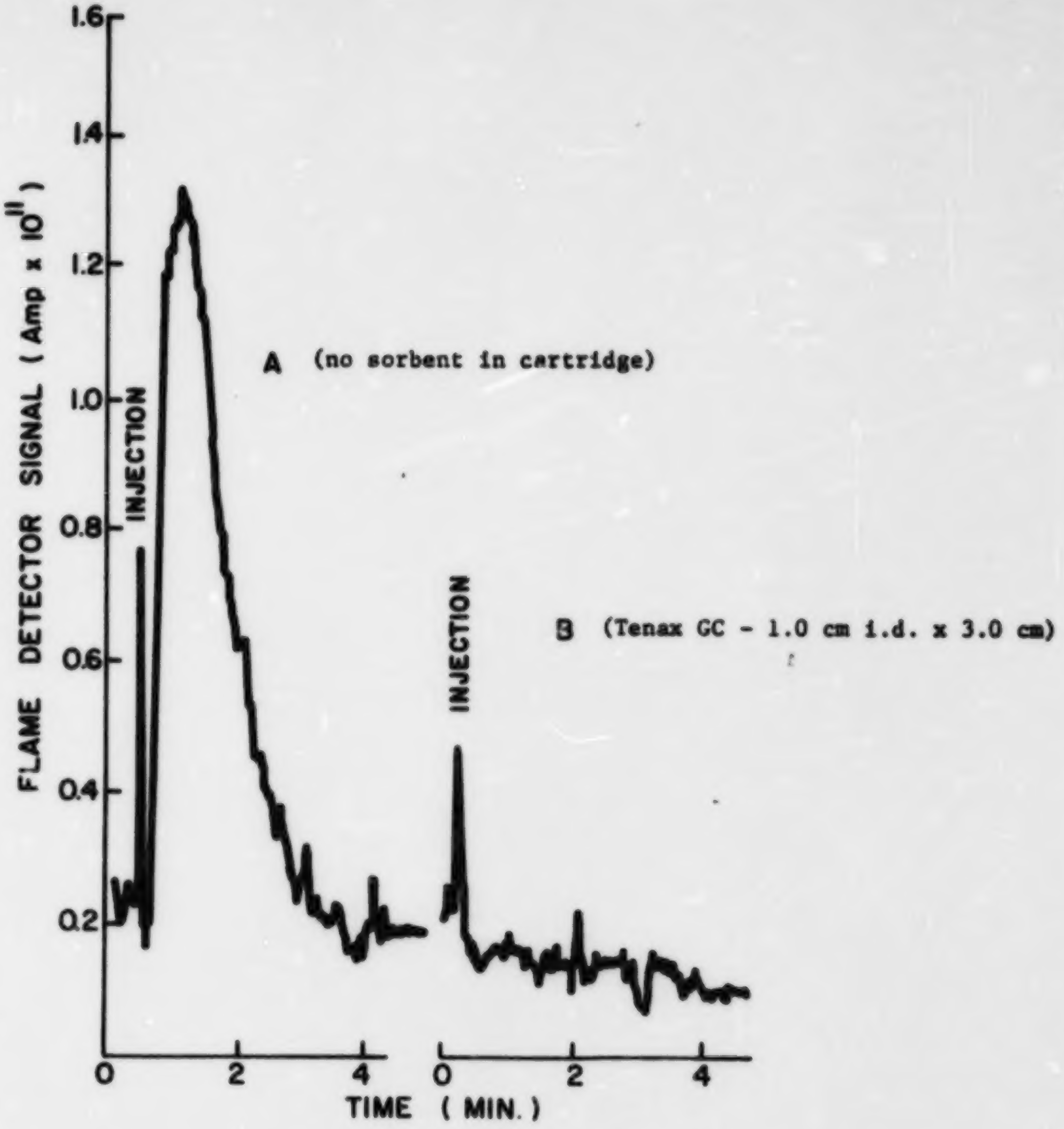


Figure 2. Elution profile of cartridge effluent. Sampling rate was 6 l/min. Test mixture III was used.

Table 4. SYNTHETIC AIR-VAPOR MIXTURES FOR CARTRIDGE SAMPLER EVALUATION

Mixture	Components[a]
I	ethyl methanesulfonate β-propiolactone [b]N-nitrosodiethylamine 1,2-dichloroethyl ethyl ether nitromethane methyl ethyl ketone[c]
II	styrene epoxide [b]N-nitrosodiethylamine butadiene diepoxide glycidaldehyde sulfolane propylene oxide
III	aniline bis-(2-chloroethyl)ether [b]N-nitrosodiethylamine Bis-(chloromethyl)ether maleic anhydride 1,3 propane sultone

[a] Approximately 300 ng of each component was used for synthesizing the air/vapor mixture.

[b] Internal standard.

[c] As decomposition product from MEK peroxide.

At 9 l/min it takes approximately one minute. Since the decay process for moderate concentrations of vapor (~0.05 ng/s) can be monitored with a flame ionization detector, the ability of a sorbent to extract vapors from a flowing gas stream was determined. This phenomenon was defined as collection efficiency, i.e. the fraction of solute vapor in the polluted gas which was retained by the sorbent bed.

The collection efficiencies for several sorbent media are given in Table 6. All of the polymeric bead sorbents were relatively effective in extracting vapors from a flowing stream of 0.25 l/min. The activated

Table 5. EXPULSION RATES FROM CHAMBER AT SPECIFIED FLOWS

	Concentration (ng/l) remaining in chamber				
Time elapsed, min	0.25 ℓ/m	4 ℓ/m	6 ℓ/m	8 ℓ/m	9 ℓ/m
0	1800	3000	3000	3000	3000
1	1588	406	149	54.9	33.3
2	1402	54.9	7.4	1.0	0.4
3	1238	7.4	0.37	0.02	0.004
4	1092	1.0	0.02		
5	964	0.14			
10	516	0.056			
20	148				
30	42				

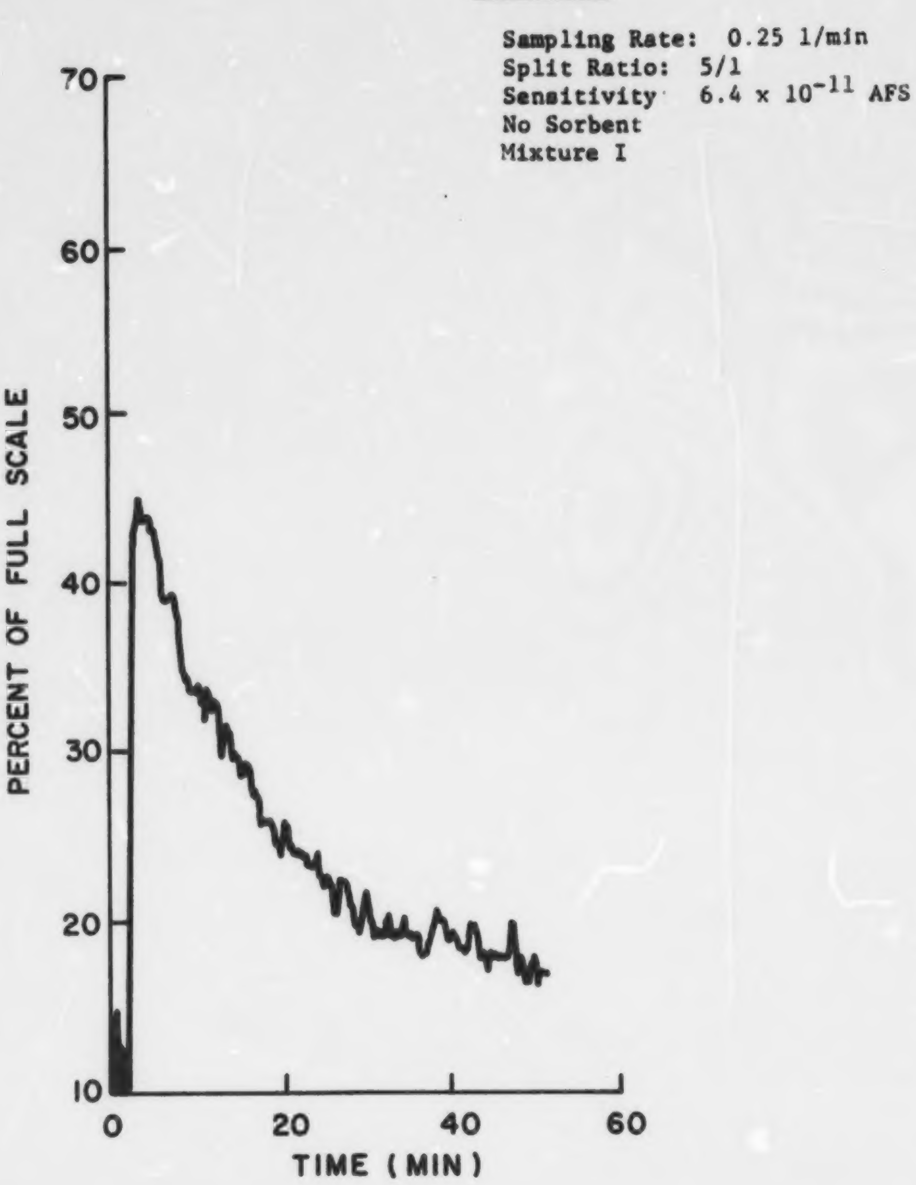
carbons were highly efficient in trapping the constituents in mixture I (see also figures 3-5); however, they were relatively ineffective when tested with mixtures II and III. In separate experiments it was discovered that propylene oxide and butadiene diepoxide were not effectively trapped by two of the cocoanut type carbons and thus accounted for the low collection efficiencies for synthetic air/vapor mixture II. A comparison of several liquid phases coated on solid supports revealed a considerable decrease in the trapping efficiency when the polarity of the phase was increased (carbowax 600 vs tricresyl phosphate). These results suggested that the more non-polar vapors are not forming a "solution" with the polar liquid phases (absorption via "like dissolves like") as readily as might be expected if polar vapors were tested. A discrimination in the

Table 6. COLLECTION EFFICIENCIES OF CANDIDATE SORBENTS

	Sorbent	Chemical Type	Percent Efficiency[a]		
			Mixture I	Mixture II	Mixture III
Polymer Beads	Tenax GC	2,6-diphenyl-p-phenylene oxide	95	90	80
	Porapak Q	polyalkyl styrene	90	95	90
	Chromosorb 101	Styrene-divinyl benzene	95	95	95
	Chromosorb 104	acrylonitrile-divinyl benzene	98	90	80
Carbons	Activated carbons	PCB cocoanut (Pittsburgh Act.)	90	95	90
		BPL coal (Pittsburgh Act.)	90	90	--
		SAL9190 cocoanut (Barneby Cheney)	90	30	--
		580-26 Cocoanut/pecan (Barneby-Cheney)	95	30	--
Liquid Phases	20% Carbowax 600 on Chromosorb W(HP) 100/120 mesh		90	90	90
	[b]Carbowax 400/Poracil C 100/120		90	90	95
	[b]Oxypropionitrile/Poracil C 80/100		98	96	90
	25% Didecyl phthalate on Chrom P 100/120		50	80	50
	20% Tricresyl phosphate on Chrom W(HP) 100/120		20	20	20

[a] Sampling rate was 0.25 l/min, packing bed dimensions were 1.056 cm I.D. x 3.0 cm in length. The exponential dilution flask was maintained at 50°C.

[b] Chemically bonded phases.



Parameters

Sampling Rate: 0.25 l/min
Split Ratio: 5/1
Sensitivity 6.4×10^{-11} AFS
No Sorbent
Mixture I

Figure 3. Elution Profile for Synthetic Air/Vapor Mixture I from Spherical Chamber (Empty Cartridge)

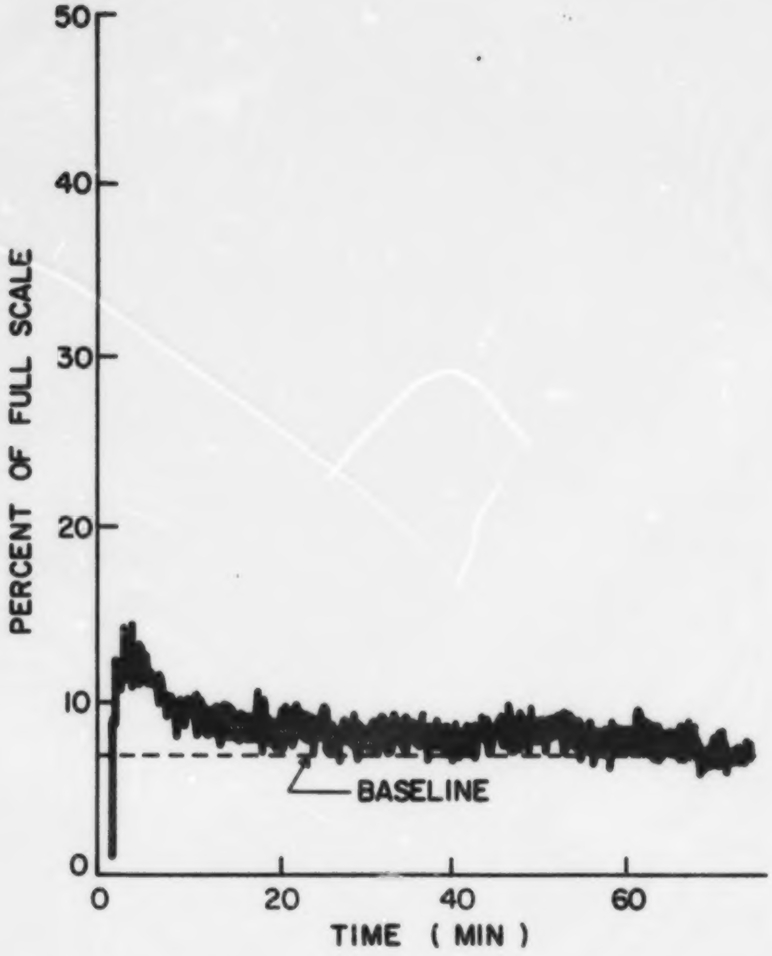
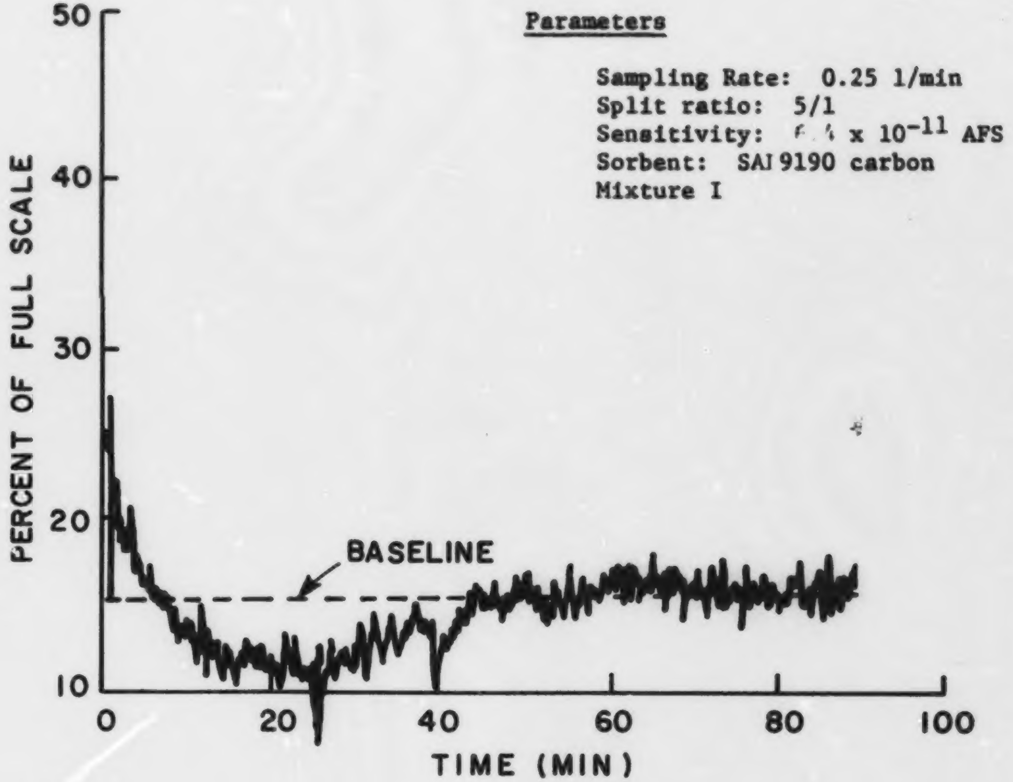


Figure 4. Collection efficiency profile for BPL carbon using test mixture I. Sampling rate was 0.25 l/min; sensitivity was 6.4×10^{-11} AFS.



Parameters

Sampling Rate: 0.25 1/min
Split ratio: 5/1
Sensitivity: 6.4 x 10^{-11} AFS
Sorbent: SAI 9190 carbon
Mixture I

Figure 5. Collection Efficiency Profile for SAI 9190 Carbon Using Test Mixture I

in the affinity and therefore trapping of chemical classes may be possible with these media; a desirable feature since the final resolution would be somewhat simplified.

Upon reviewing the collection efficiencies for candidate sorbent media, and the results from thermal desorption experiments (Section VII) two polymeric beads, Tenax GC and Chromosorb 101, were selected and further tested at higher flow rates. As shown by the data in Tables 7 and 8 high collection efficiencies were also obtained at rates up to 9 l/min.

The described monitoring system can be also used to determine the effects of continuous sampling when no additional solute vapors are present in the air stream. This represents the extreme case encountered during field sampling. When polluted gas enters a sorbent bed an equilibrium zone is established near the point of entry. As more pollutant is introduced this zone may expand through the packing length until the

Table 7. APPROXIMATE COLLECTION EFFICIENCY FOR TENAX-GC AT VARIOUS SAMPLING RATES

	Sampling Rate (l/min)			
Test Mixture[a]	4	6	8	9
I	95[b]	90	90	90
II	95	95	90	90
III	>95	95	95	95

[a] Approximately 1500 ng/component/mixture was used to determine efficiencies. Packing dimensions were: 10.5 mm x 60 mm, Mesh 60/80. The exponential dilution flask was maintained at 50°C.

[b] All values are average of duplicate runs.

Table 8. APPROXIMATE COLLECTION EFFICIENCY FOR CHROMOSORB 101 AT VARIOUS SAMPLING RATES

	Sampling Rate (l/min)			
Test Mixture[a]	4	6	8	9
I	95[b]	95	90	95
II	>95	95	95	90
III	>95	95	90	80

[a] Approximately 1500 ng/component/mixture was used to determine efficiencies. Packing dimensions were: 10.5 mm x 30 mm, 100/120. Exponential flask was at 50°C.

[b] All values are average of duplicate runs.

capacity of the sorbent is exceeded. However, if after an initial period of time no additional polluted vapors are introduced and purging of the packing bed continues, the zone of vapors may move through the packing bed. When the mass zone moves to the end of the available packing bed and the vapors begin to leave, breakthrough has occurred. Furthermore, the elution volume (EV) can be calculated if the time required for the zone to traverse and elute from the sorbent bed and sampling rate are known. In an ideal system, EV has an infinite value. An investigation of EV is presented later in this section.

The amount of vapor adsorbed to a given quantity of adsorbent depends on the pressure, temperature and concentration of the solute vapor[54]. The higher the pressure or concentration, the greater the amount adsorbed. When an adsorbent and solute vapor are placed in contact with each other, an equilibrium is reached between adsorption and desorption. If the concentration of the vapor increases or decreases, the mass of adsorbed vapor also increases or decreases to establish a new equilibrium value. This is an important phenomenona during the collection of vapors from a flowing stream; the binding affinity of the adsorbent for the solute must be very high in order that the sampling rate to be relatively independent of collection efficiency. The data presented in this section supports this viewpoint.

The attractive forces of atoms or molecules responsible for adsorption on the surface of a solid are attributed generally to two phenomena: physical and chemisorption. Physical adsorption is primarily due to van der Waal's forces which is similar to the condensation of a gas. The magnitude of the heat evolved during adsorption and gas condensation are similar. The quantity adsorbed may be several monolayers. When the pressure of the vapor or its concentration is lowered, a subsequent decrease in physical adsorption is observed. In contrast, chemisorption is not readily decreased and only a monolayer of solute vapor is adsorbed on the surface. Also, the heat evolved during chemisorption is much larger than in physical; a surface compound is formed.

Langmuir[55,56] advanced a model theory of adsorption which regards the surface of a solid to be homogeneous, i.e., that the sites on the surface all exhibited equivalent affinity for the solute vapor, and each site was independent of another. However, surfaces are known to be heterogeneous. The Langmuir equation is represented as follows:

$$c/q = 1/Kb + c/b \qquad (2)$$

where c = concentration of solute (m/l)

q = moles of solute adsorbed per gram of adsorbent

b = moles of solute vapor adsorbed per gram of adsorbent

K = equilibrium constant for $V + S \rightleftharpoons VS$

The complex VS represents the fraction of adsorbent sites occupied by vapor molecules (V), and V is the fraction of free sites. At a given value of q, V and VS are constant and equation (2) reduces to

$$K' = 1/c$$

Thus, the enthalpy of adsorption, $\Delta H°$, may be calculated by plotting 1/c vs 1/T at a given q value:

$$\Delta H° = \frac{2.303RT_1T_2}{T_2-T_1} (\log K'_2 - \log K'_1) \qquad (3)$$

The Clausius-Clapeyron equation (3) can be used to calculate the heat of desorption. A larger amount of heat is required to desorb a mole of gas when only a small fraction of the surface is covered than when a large fraction of the surface is covered; indicating inhomogeneity of the surface.

Since adsorption affinity constants are strongly temperature dependent, the effects of temperature should be considered in any collection efficiency and breakthrough study. We are currently examining the influence of temperature and humidity on the collection efficiency of Tenax GC and Chromosorb 101 using the monitoring system described here. The monitoring system is also amenable to studies of humidity and temperature and their effects on sorbent trapping performance. Calibrated humidity levels can be introduced into the chamber or can be heated with a heating mantel for simulation of high temperature and humidity as observed in field conditions.

With respect to bed dimensions (length and i.d.) and particle size, it has been suggested that they play no major role on breakthrough[20]; however our preliminary studies have shown that an increase in both collection efficiency and EV can be expected. These relationships need to be defined more closely.

Displacement chromatography may occur during sampling of polluted air leading to early breakthrough. Because each substance has a specific affinity for the sorbent, the quantity adsorbed is characteristic for each substance; furthermore one compound can be displaced by another, if the latter has a higher adsorption affinity. Thus, breakthrough studies should be performed in the field under the full complexity of polluted air rather than in the laboratory. These results are discussed below.

The capacity of Tenax GC for various compounds such as alkanes, alcohols, and amines have been reported to be higher than for aldehydes, ketones, and phenols[17]. Bertsch et al.[17] also reported that all sulfur compounds examined were trapped in a narrow zone at the cartridge entrance. Volatile hydrocarbon compounds containing less than five carbon atoms are not efficiently trapped by Tenax GC[17] while aromatics were[17].

RELATIONSHIP BETWEEN SAMPLING RATE AND CARTRIDGE PRESSURE DIFFERENTIAL

Most of the design principles that have been developed for the efficient use of sorbents have been prescribed for the removal of vapors from air to improve its quality. For example, Jones[15] discusses the most efficient physical arrangement of a charcoal bed to remove benzene vapor from air. His design presumes a steady flow of air of uniform concentration, with the gradual accumulation of vapor until the sorbent becomes saturated and breakthrough occurs (frontal elution).

However, additional criteria were considered in this problem during the design of a sampling system which is based upon a cartridge concept for the collection and analysis of trace organic vapor pollutants. The most important factors are revealed in the aerodynamic features of the cartridge, specifically the pressure differential, ΔP, produced across a specified sorbent bed. The pressure differential is related to (1) the air flow-rate, (2) the cartridge shape (diameter and depth of packing), (3) the particle size distribution, (4) the particle shape, and (5) to a lesser extent upon the air temperature and humidity. Since ΔP is an important ingredient for relating the power requirement of a field sampler (Section VIII) to sampling rate and duration, it was carefully investigated in this program.

Experimental

An equation was derived from the mechanical energy balance and Leva's correlation[53] to predict ΔP which was valid at isothermal flow:

$$P_1^2 - P_2^2 = \frac{2ZRG^2T}{g_cM} \left[\ln \frac{V_2}{V_1} + \frac{2fm\ (1-\varepsilon)^{3-n} L}{\phi_s^{3-n}\ \varepsilon^3 D_p} \right] \qquad (4)$$

where p_1 = pressure at inlet to sampler, N/cm^2

p_2 = pressure at outlet of sampler, N/cm^2

Z = gas compressibility factor (air = 1)

R = gas constant, 831467 N x cm/kg moles x °K

G = fluid mass velocity, kg/sec x cm^2

T = absolute temperature, °K

g_c = conversion factor, force to mass, kg x cm/N x sec

M = molecular weight of gas flowing, kg/mole

V_1 = specific volumes of gas at inlet, cm^3/kg

V_2 = specific volume of gas at outlet, cm^3/kg

fm = modified friction factor for flow through packed solids

ε = bed void fraction

ϕ = particle shape factor = $V^{2/3}/0.205$ x surface area

D_p = particle diameter of packing, cm

L = depth of sampler packing, cm

The particle diameter (Dp) can be calculated as $1/(\Sigma x/dp)$, where x is the mass fraction with size d_p and

$$d_p = (d_1 \times d_2)^{0.5}$$

The minimum and maximum openings of adjacent sieves are designated as d_1 and d_2. In the above equation, the mass-force conversion factor, gas compressibility factor, and upstream and downstream specific gas volumes are represented by g_c, Z, V_1 and V_2, respectively.

For the computations, Z and ¢ were set equal to unity, n and fm were evaluated as functions of the Reynolds number (particle diameter x mass air rate/air viscosity), and E was evaluated as a function of the ratio particle diameter/tube diameter. Because of the relatively small magnitude of $\ln(V_2/V_1)$, it was omitted. All calculations were programmed and executed on an IBM 360/70 computer at the Triangle Universities Computation Center, Research Triangle, N. C.

Results and Discussion

Figures 6-8 depict computer generated pressure differentials for three different sorbent particle ranges (12/30, 35/60, and 100/120) and one set of cartridge dimensions. It was evident from these data that ΔP increased exponentially as the flow rate was increased. Recalling that 10.03 Newtons/cm^2 is equivalent to 760 mm Hg, then a flow rate of 5 l/min produced a ΔP of 11.4 mm Hg (Fig. 6) for a mesh range of 12/30. On the other hand, to achieve the same flow rate with mesh ranges of 35/60 and 100/120 (Fig. 2 and 3) a ΔP of 68.4 and 228 mm Hg, respectively would be produced.

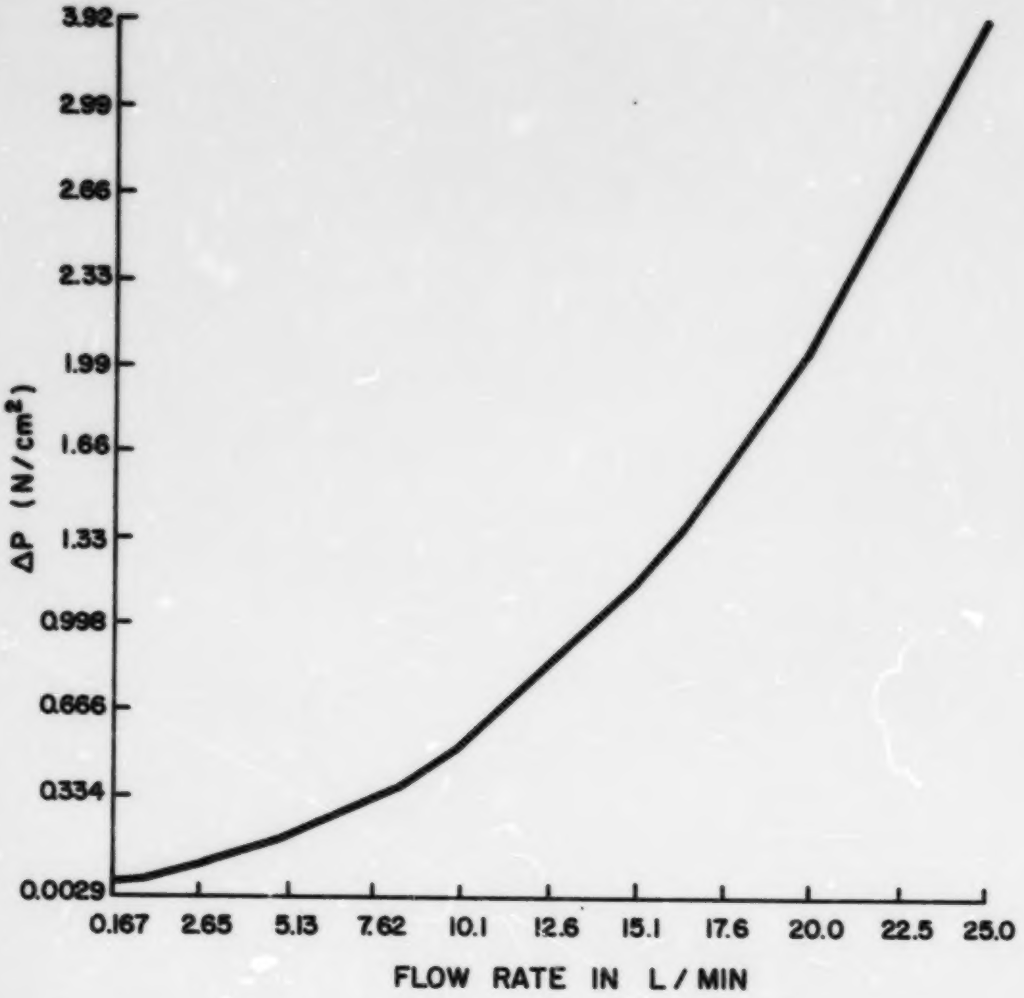


Figure 6. Calculated pressure differential for 12/30 mesh particles. Cartridge dimensions were 1.056 cm i.d. x 3.0 cm in length.

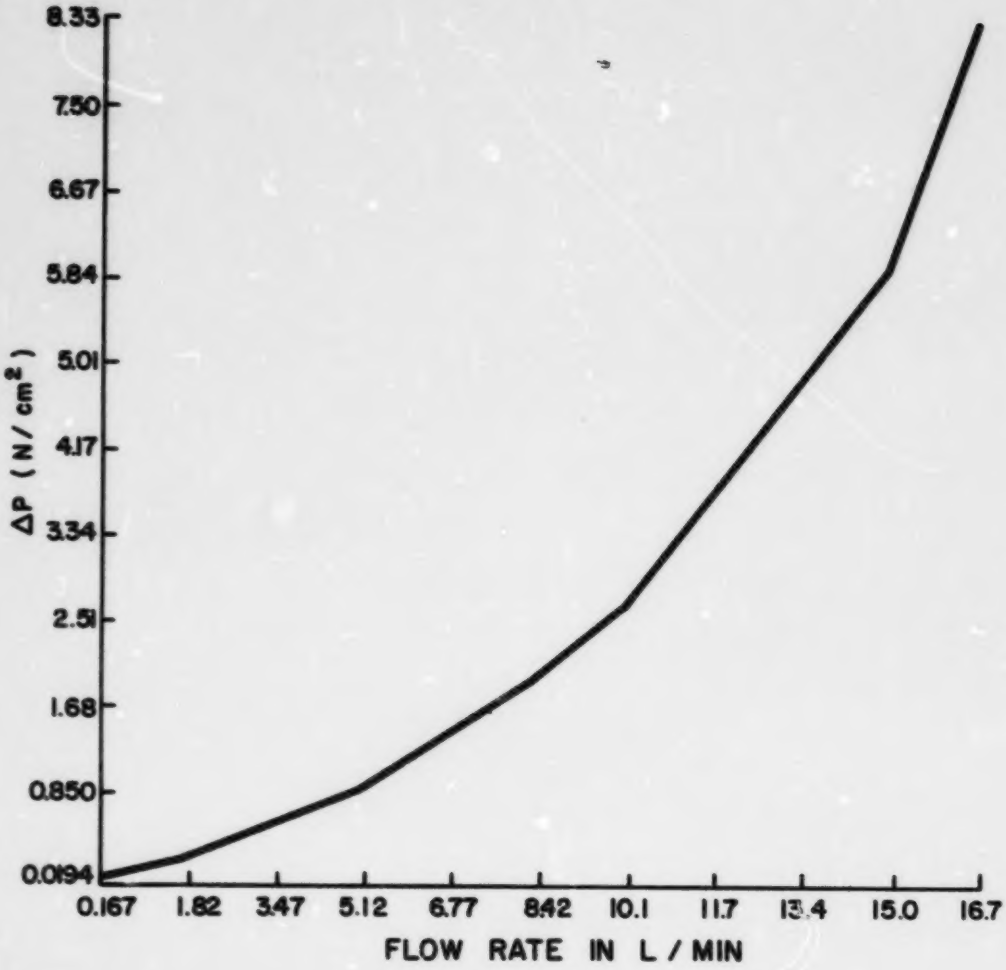


Figure 7. Calculated pressure differentials for 35/60 mesh particles. Cartridge dimensions were 1.056 cm i.d. x 3.0 cm in length.

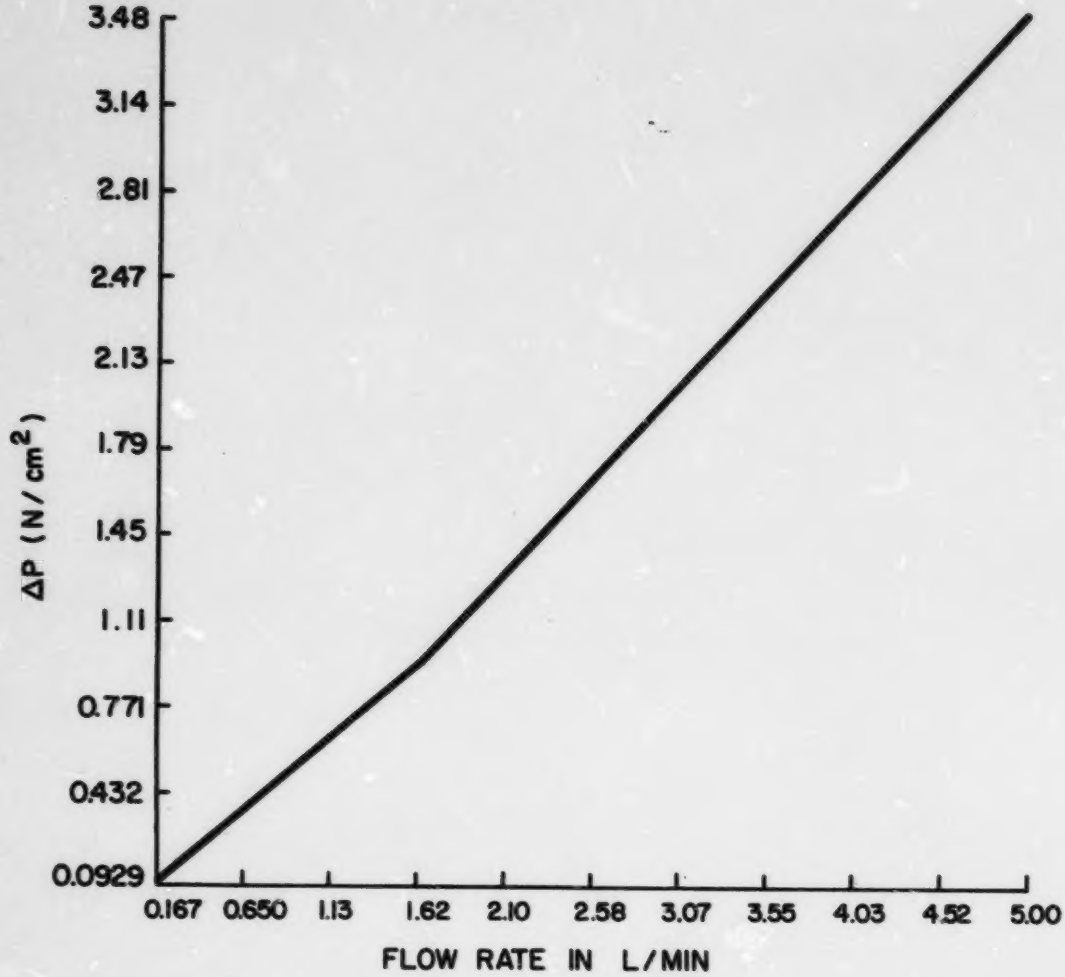


Figure 8. Calculated pressure differential for 100/120 mesh particles. Cartridge dimensions were 1.056 cm i.d. x 3.0 cm in length.

The calculated pressure drop curves for each mesh size allows some judgement to be made with respect to the practical attainable flow rates for each of these mesh sizes, and the most suitable bed packing dimensions which will allow the attainment of desired field sampling rates. Furthermore, large ΔP values were undesirable since vacuum desorption ("stripping") of vapors initially trapped on a sorbent would occur if a sampling system was used whereby the air sample was drawn through the cartridge. This situation would thus seriously affect the collection efficiency and no doubt breakthrough (elution volume decreased) would occur prematurely. A pumping system which forces the air through the cartridge would be preferrable for these reasons.

In addition to deriving a function which would allow ΔP to be predicted under a variety of conditions, ΔP was experimentally determined to establish the validity of equation (1). The pressure differential was measured for air either drawn or forced through the cartridge containing sorbent. Figure 9 compares ΔP values which were calculated assuming an average particle diameter, $\bar{D}_p$, of 0.0211 cm to the experimentally determined for a sorbent with a 60/80 U.S. mesh range. This data demonstrates a good correlation between ΔP values calculated using equation (1) and those experimentally measured; however, for exact calculation of pressure drop the particle size and shape must be known.

The effect of (1) bed packing diameter, (2) bed length, (3) sampling rate, and (4) particle mesh range on the pressure differential developed across a sampling cartridge was examined. These data are depicted in Figure 10-17 for air forced through the sampler. High ΔP values were experienced when cartridge diameters of 0.5 cm were tested (Figures 10, 12, and 14) at high sampling rates, even when coarse sorbent particles

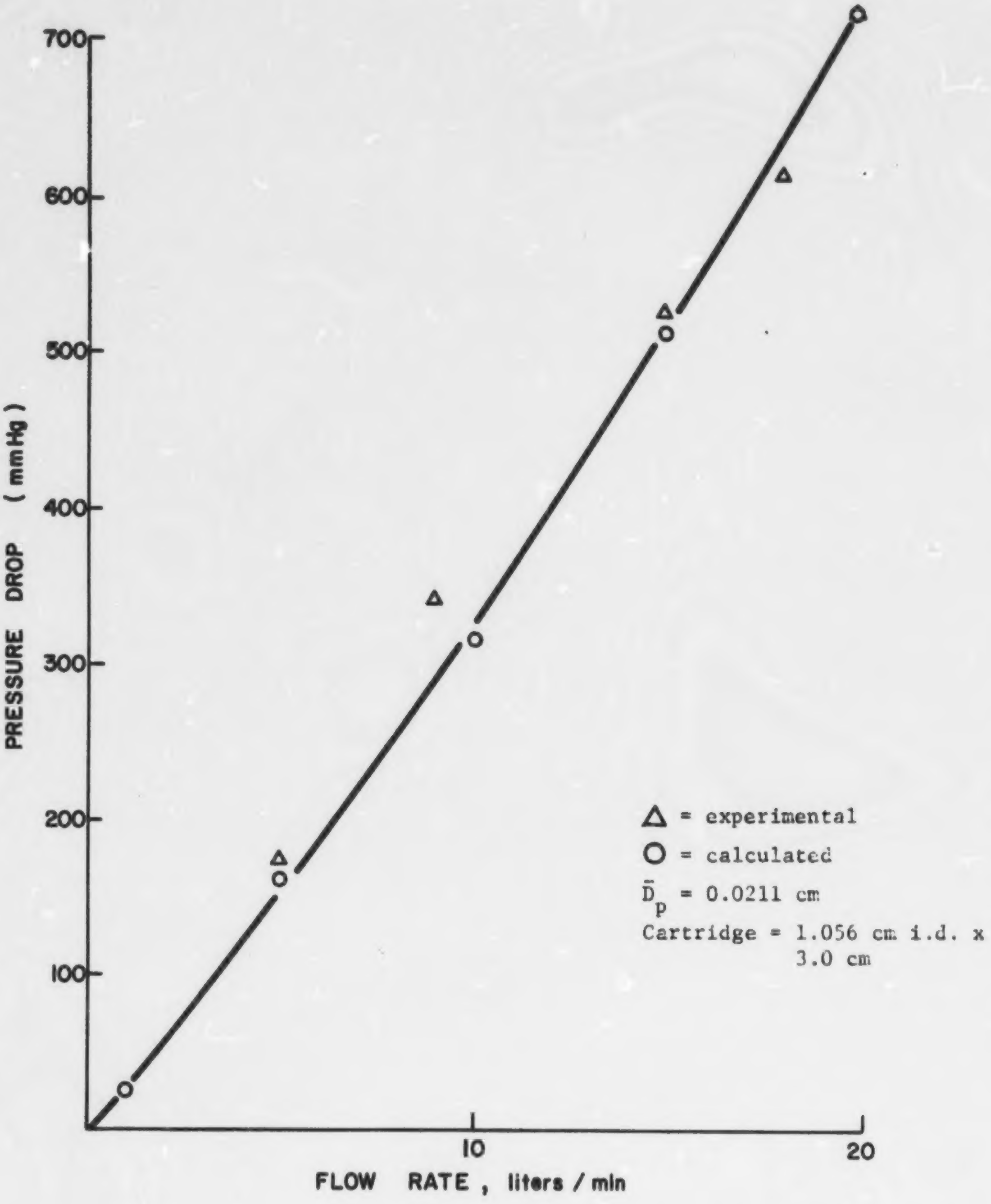


Figure 9. Comparison of calculated and experimental pressure differential for a Tenax GC (60/80) cartridge.

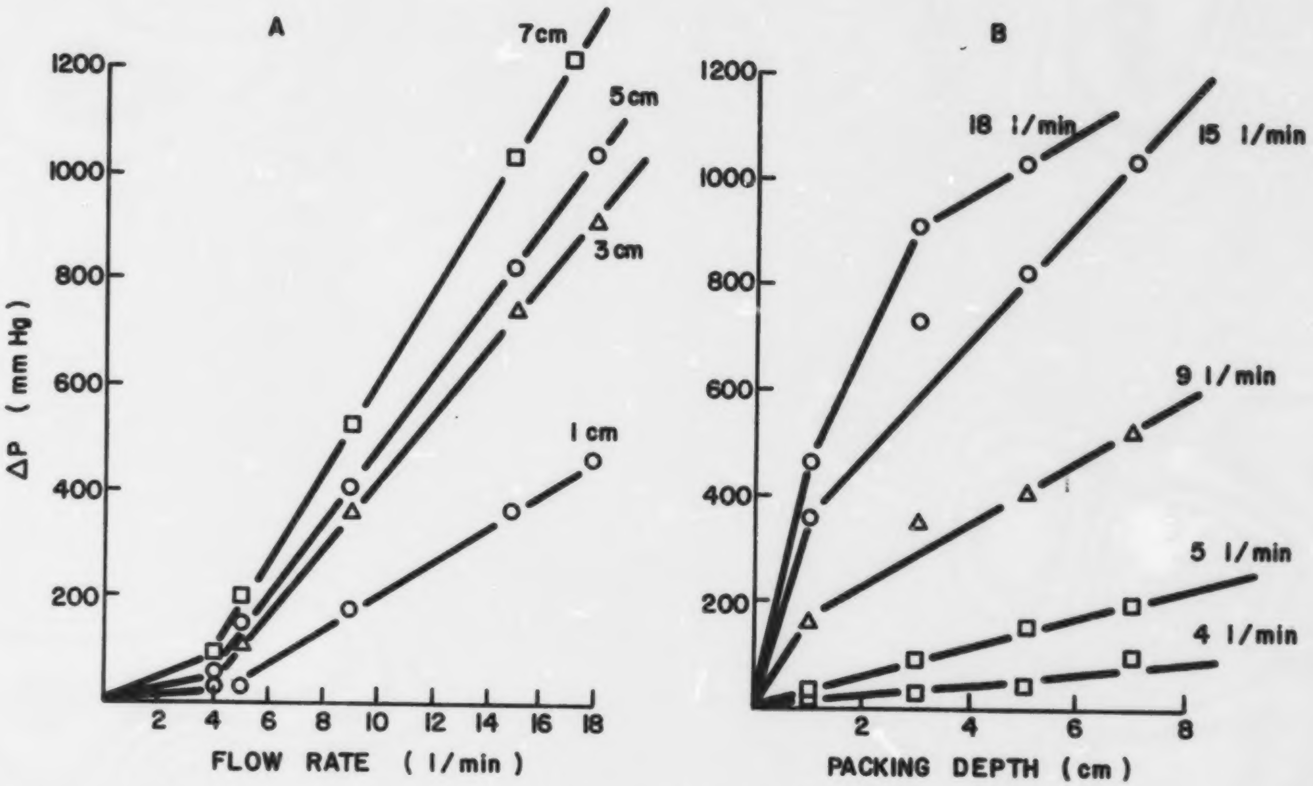


Figure 10. Pressure differentials (ΔP) for cartridges containing BPL carbon (12/30) with a cartridge i.d. of 0.5 cm.

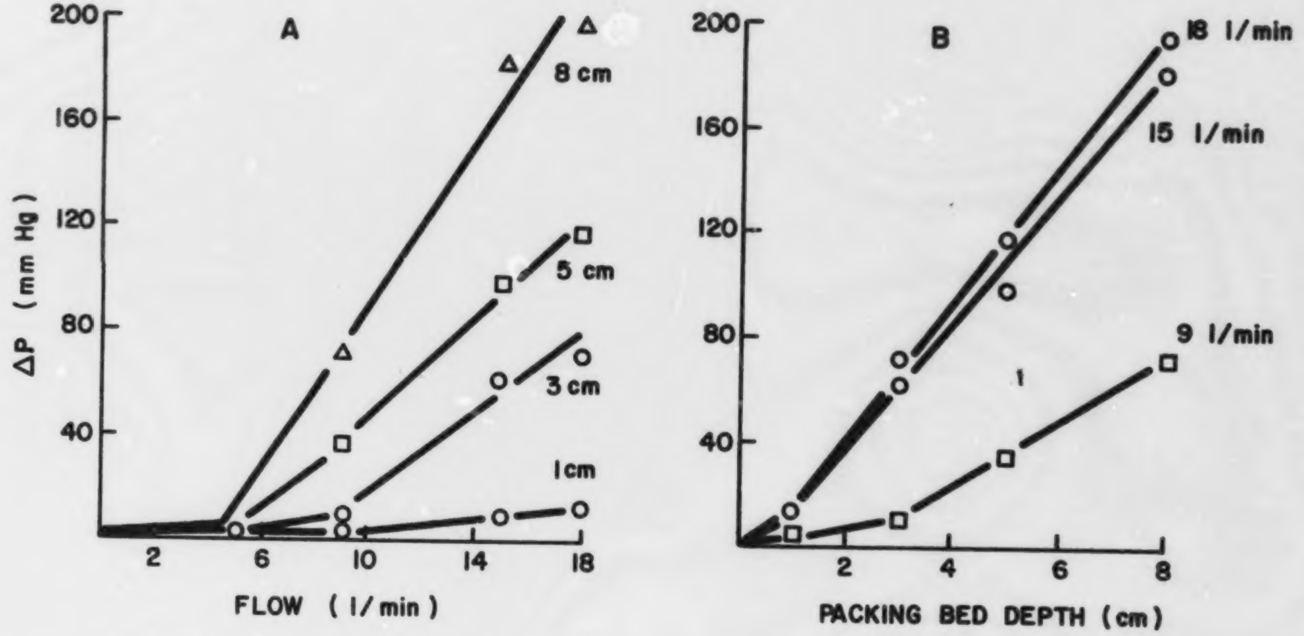


Figure 11. Pressure differentials (ΔP) for cartridges containing BPL carbon (12/30) with a cartridge i.d. of 1.056 cm.

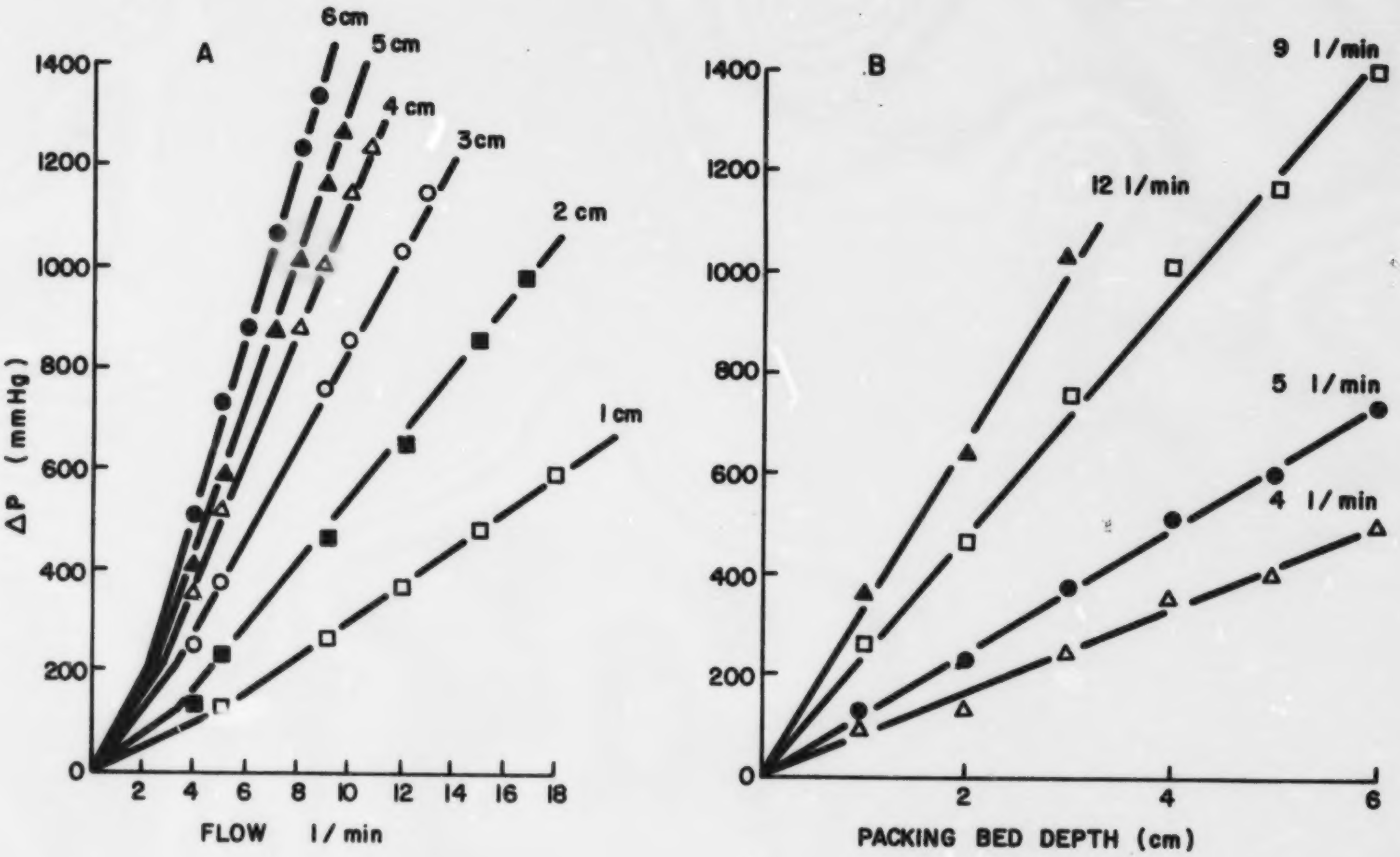


Figure 12. Pressure differentials (ΔP) for cartridges containing Tenax GC (35/60) with a cartridge i.d. of 0.5 cm.

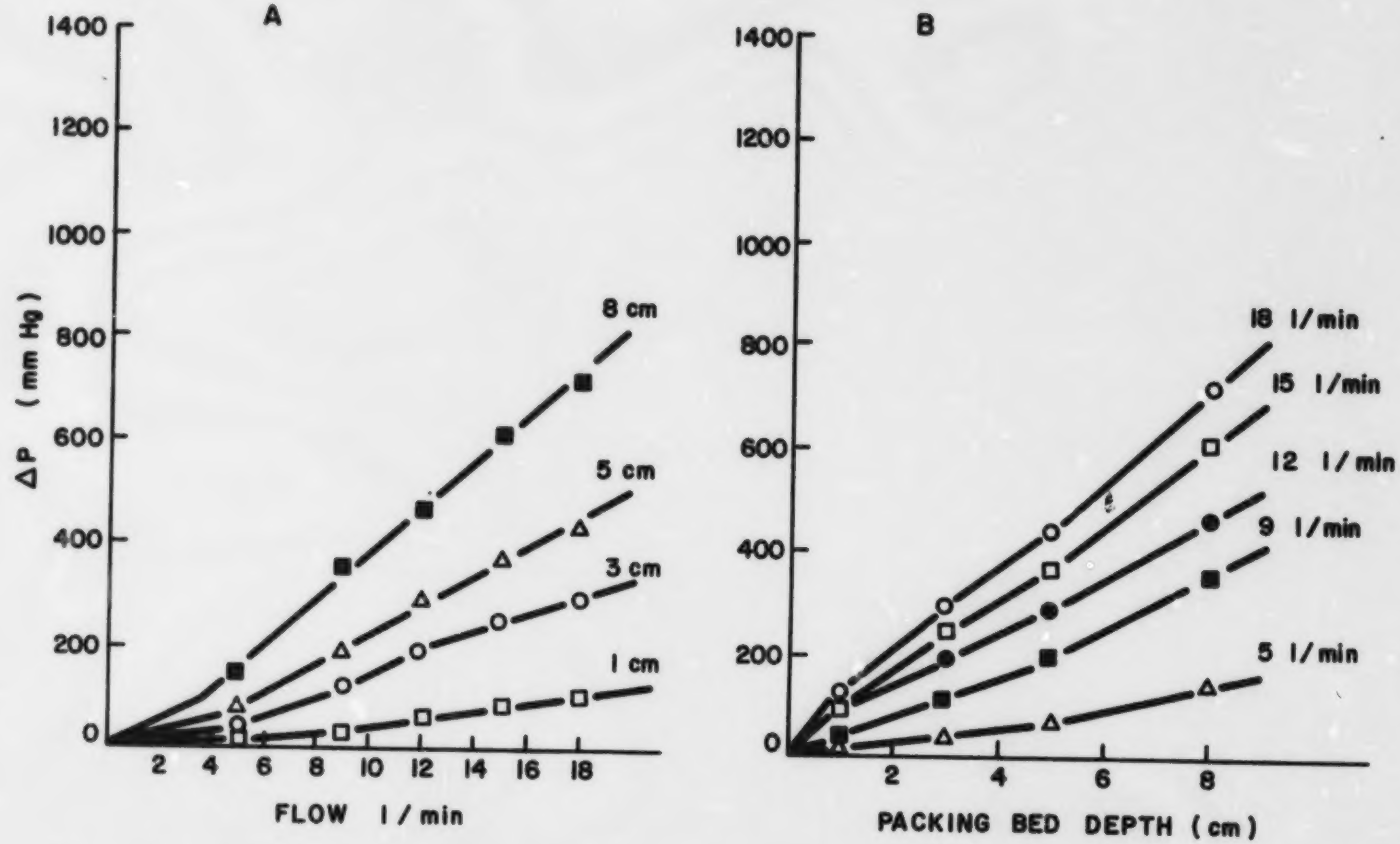


Figure 13. Pressure differentials (ΔP) for cartridges containing Tenax GC (35/60) with a cartridge i.d. of 1.056 cm.

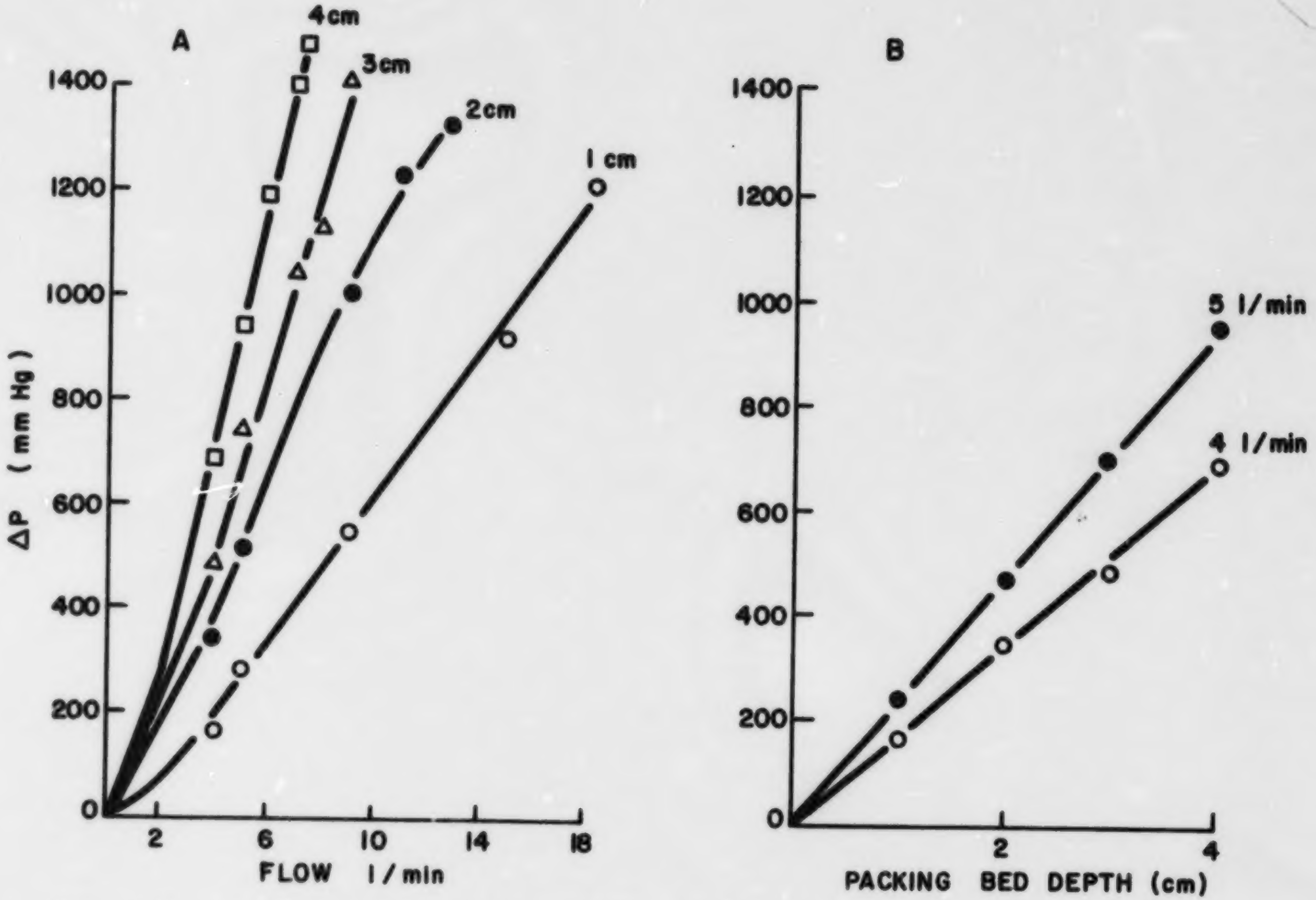


Figure 14. Pressure differentials (ΔP) for cartridges containing Tenax GC (60/80) with a cartridge i.d. of 0.5 cm.

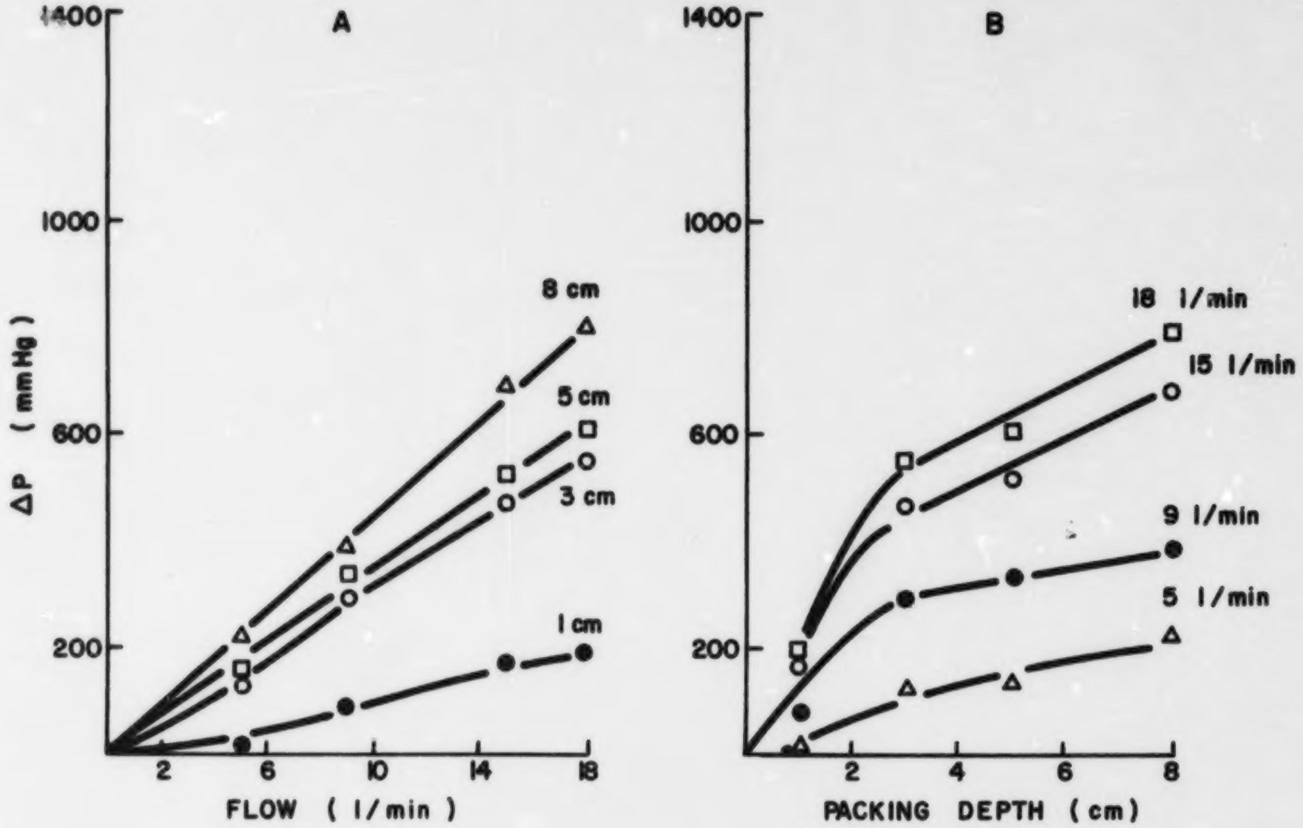


Figure 15. Pressure differentials (ΔP) for cartridges containing Tenax GC (60/80) with a cartridge i.d. of 1.056 cm.

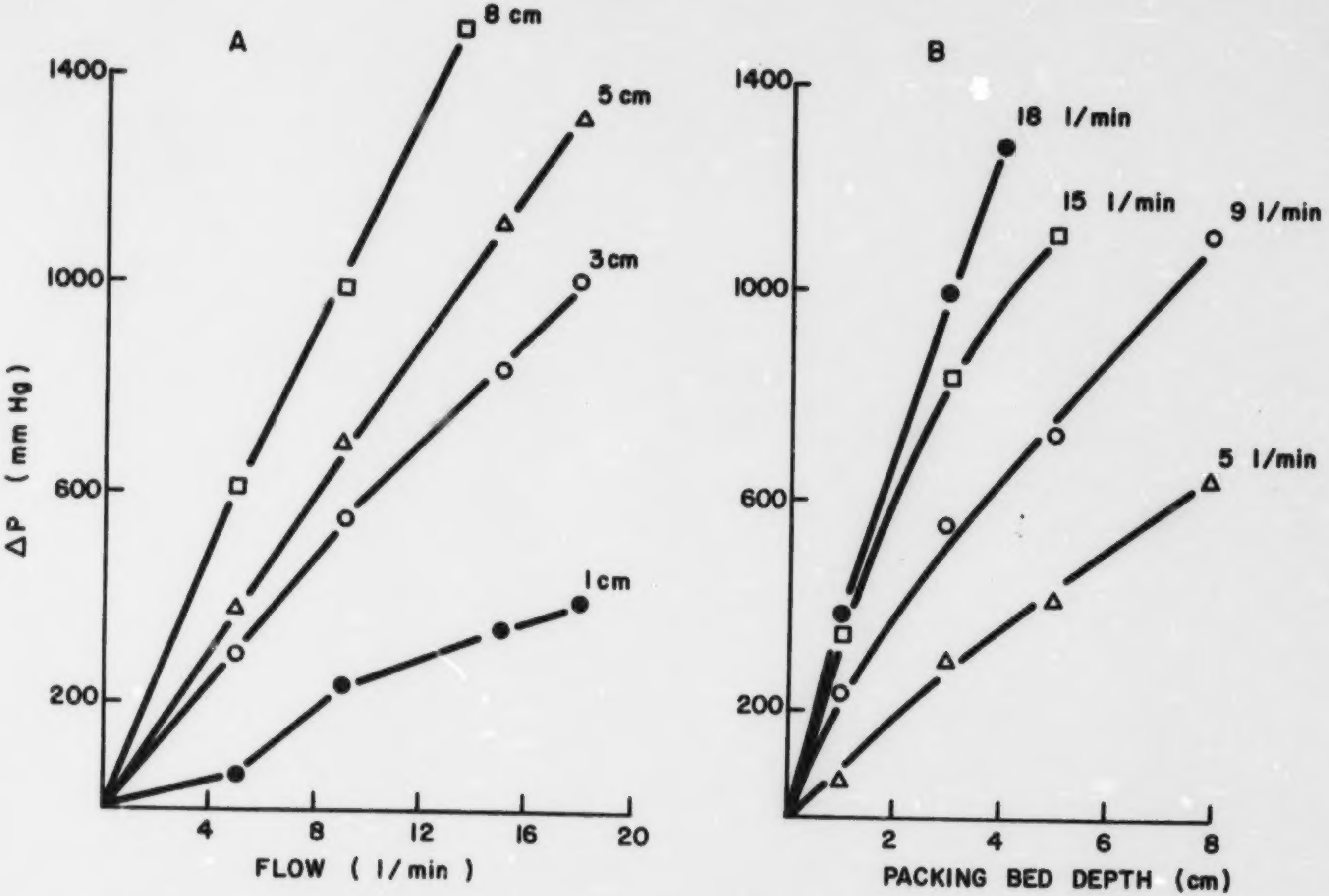


Figure 16. Pressure differentials (ΔP) for cartridges containing Chromosorb 101 (100/120) with a cartridge i.d. of 1.056 cm.

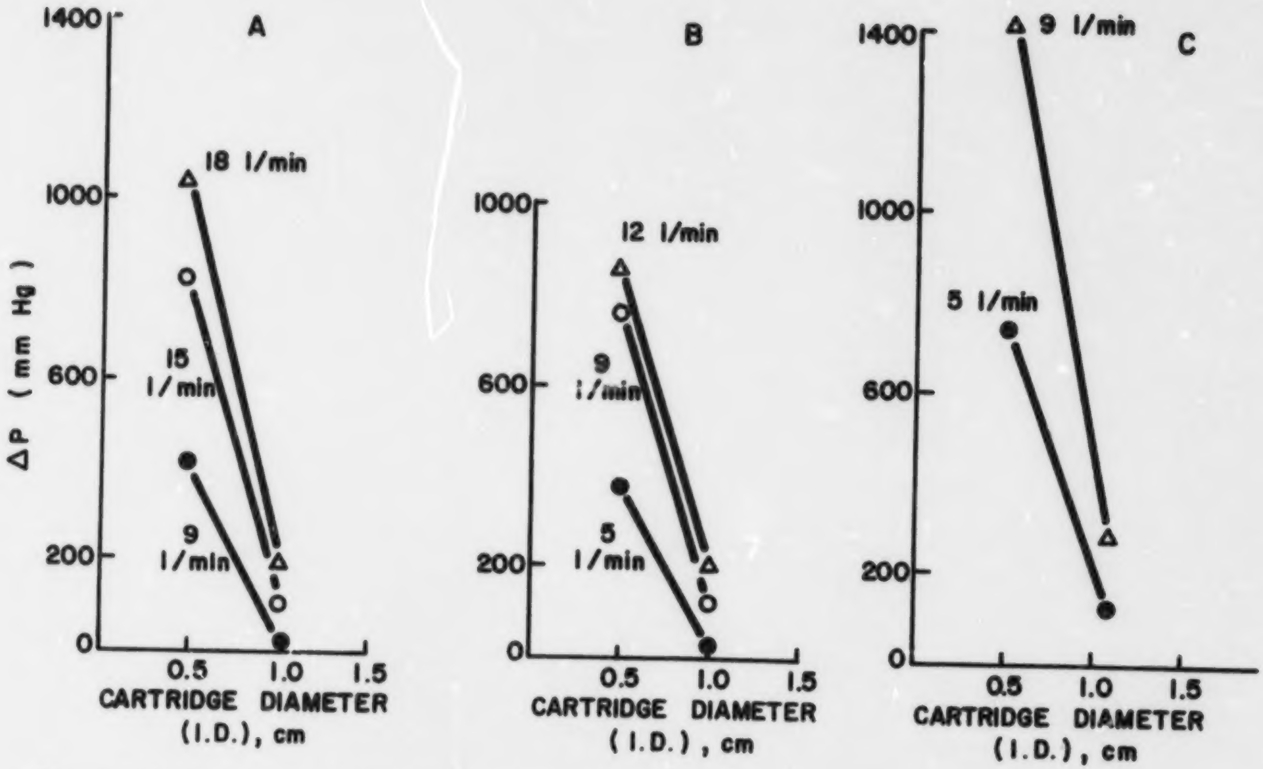


Figure 17. Effect of particle mesh range on pressure differential and relationship to cartridge diameter. BPL carbon (12/30), Tenax GC (35/60) and Tenax GC (60/80) are given by A, B, and C, respectively. Packing bed depths were 5 cm (A), 3 cm (B), and 3 cm (C).

(12/30 mesh) were used. Similarly, a mesh range of 100/120 in 1.056 cm diameter cartridges yielded large ΔP values (Figure 16). Figure 17 and 18 summarizes the effect of cartridge diameter and particle size on pressure drop respectively. At a flow of 10 l/min ΔP doubles when 35/60 and 60/80 mesh ranges are compared. It increases almost an order of magnitude from mesh 12/30 to 60/80. These data taken collectively indicated that cartridge diameters of 0.5 cm and containing mesh ranges of $\geq$ 35/60 precluded their use in any studies which would require field sampling rates > 4 l/min; likewise, a mesh of 100/120 and bed diameter of $\leq$ 1.056 cm would not be suitable.

Pressure differentials developed across cartridges while drawing air through the sampler were also measured (Figures 19-24). The general trends observed in previous ΔP experiments were also apparent in these studies. However, the restrictions on sampling rates were even greater.

ESTIMATION OF BREAKTHROUGH DURING FIELD SAMPLING

On the basis of results obtained for collection efficiencies, thermal desorption (Section VII) and pressure drop measurements, Tenax GC and Chromosorb 101 were selected for further study as possible candidate materials for collecting hazardous vapors. Field sampling experiments were designed to provide relative breakthrough data for volatile vapors, i.e. to determine when the mass transfer zone has moved to the end of the available packing bed. The estimation of elution volume required for breakthrough to occur provided a further assessment of sorbent materials and their utility for collecting carcinogenic vapors from ambient atmosphere. Furthermore, the packing bed depth required to minimize breakthrough yielded information useful for designing reliable cartridge samplers.

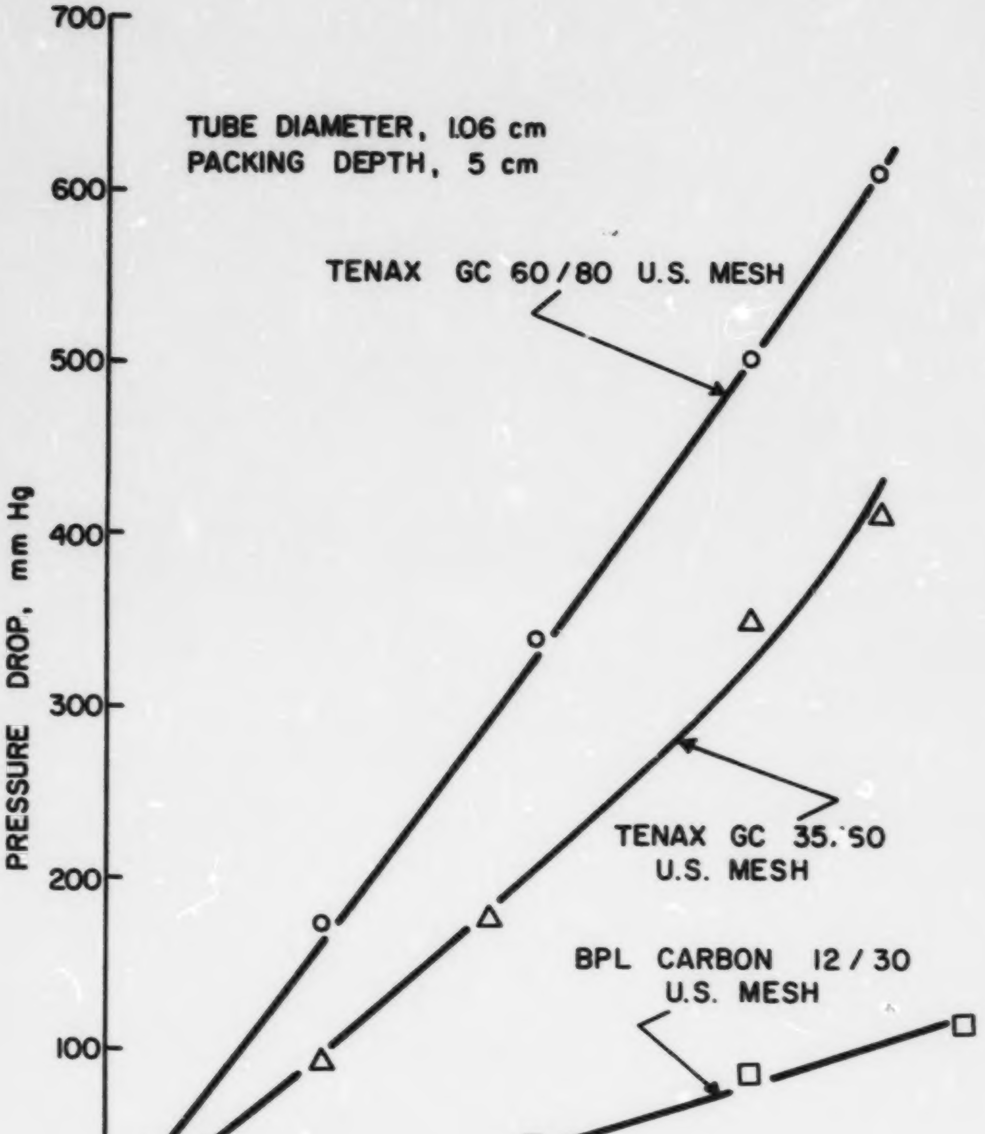


Figure 18. Effect of particle size on pressure differential.

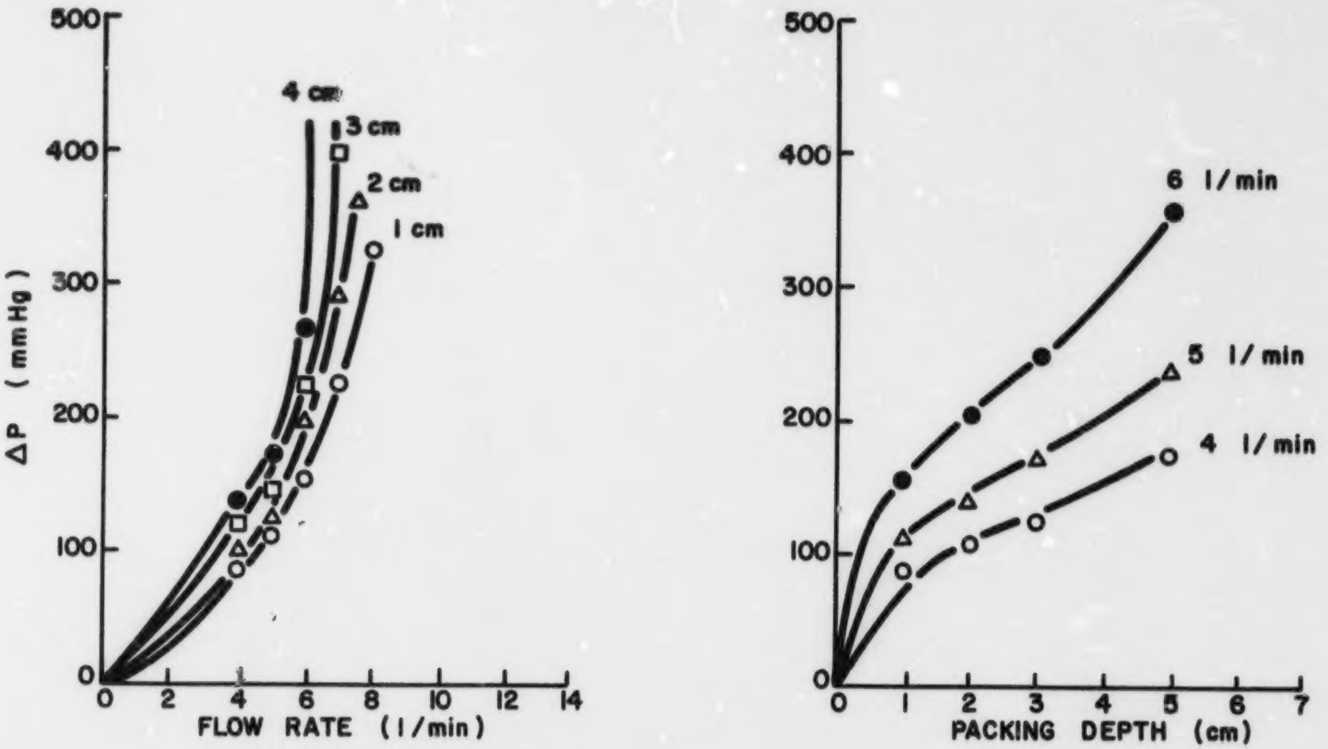


Figure 19. Pressure differential developed for BPL carbon (12/30) cartridge with an i.d. of 0.5 cm during vacuum sampling.

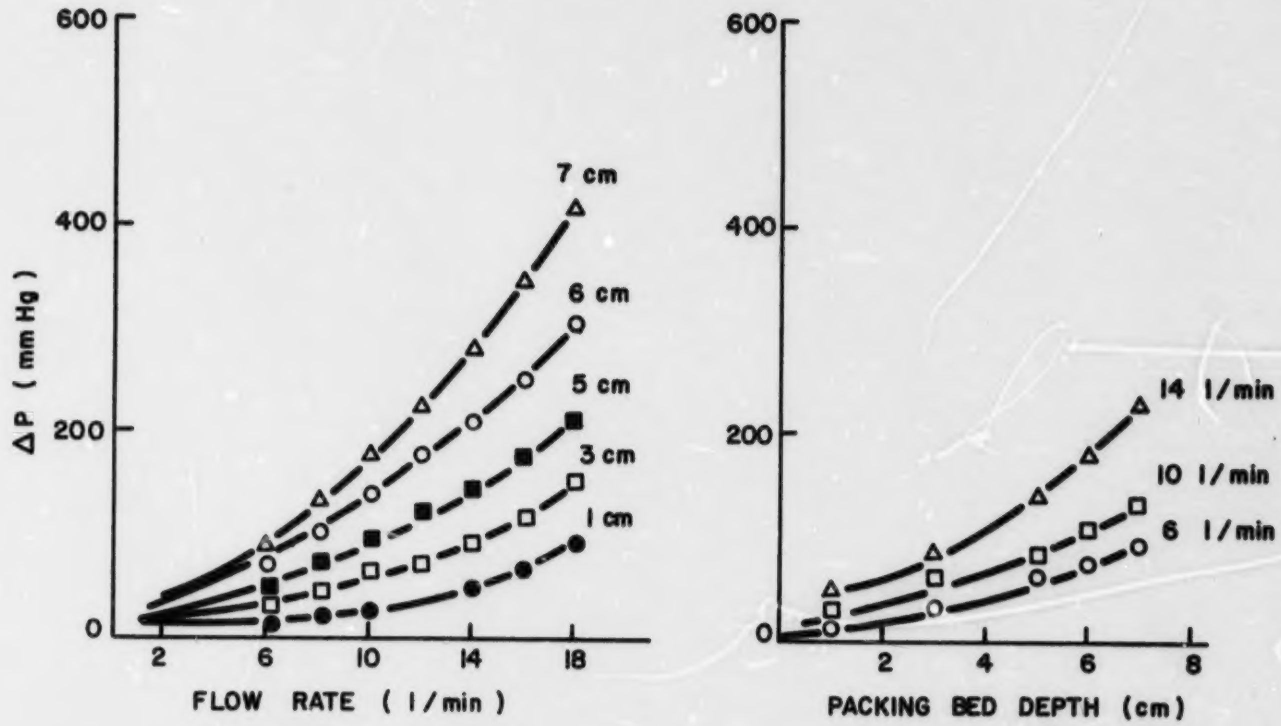


Figure 20. Pressure differentials for BPL carbon (12/30) for air drawn through a 1.056 cm i.d. cartridge

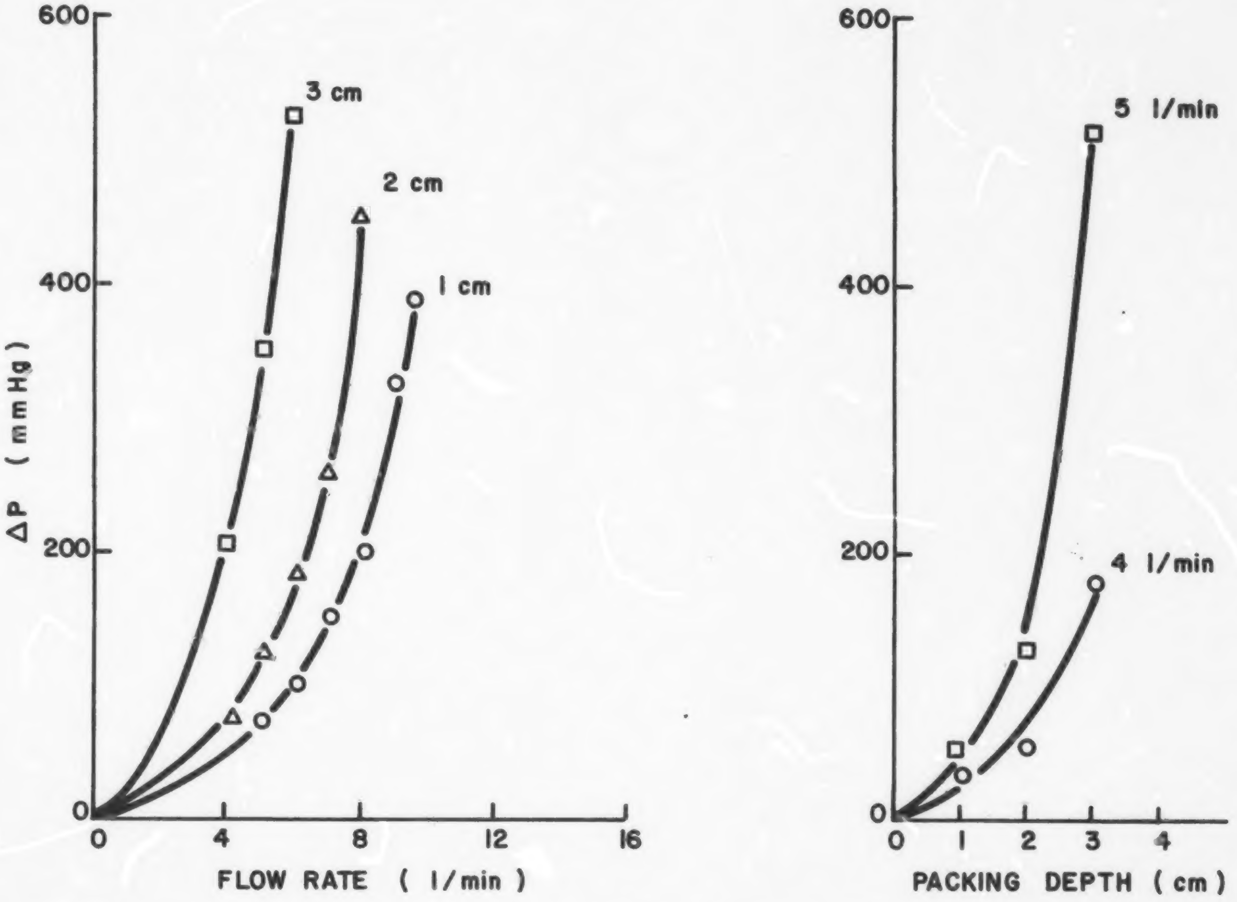


Figure 21. Pressure differential developed for Tenax GC (35/60) cartridge with an i.d. of 0.5 cm during vacuum sampling.

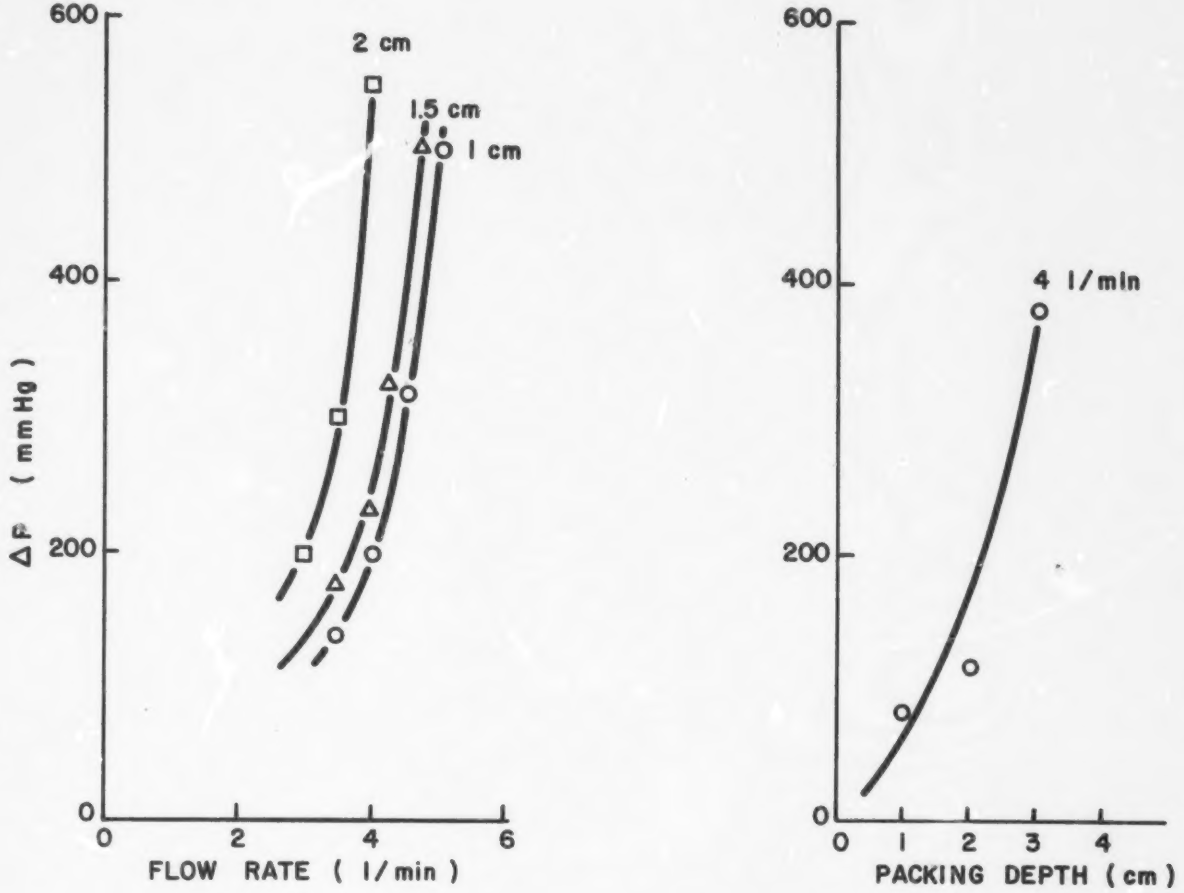


Figure 22. Pressure differential developed for Chromosorb 101 (60/80) cartridge with an i.d. of 1.056 cm during vacuum sampling.

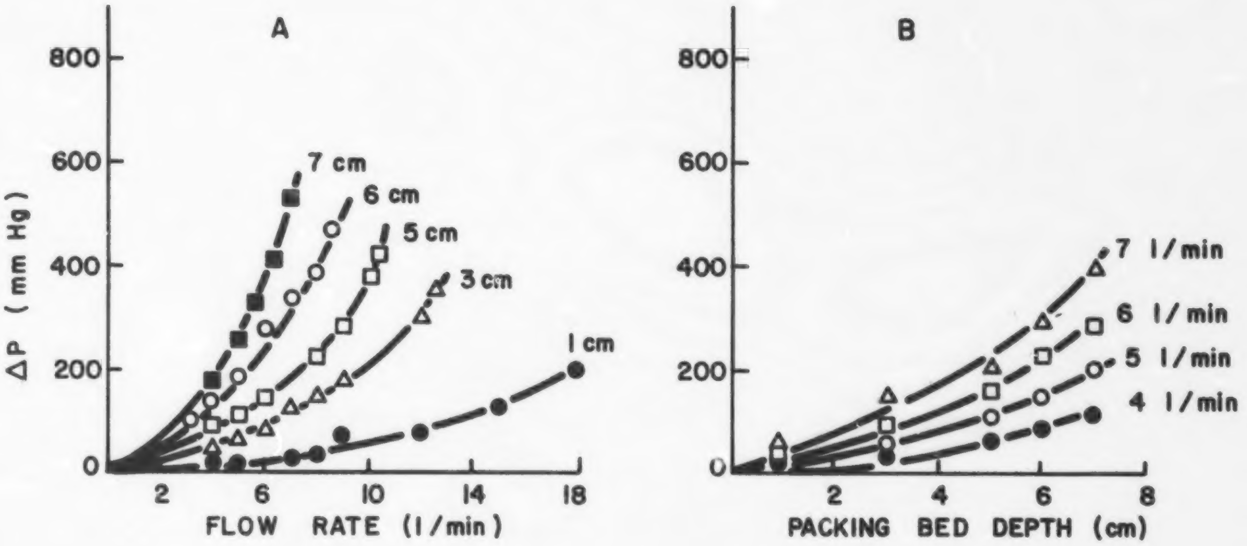


Figure 23. Pressure differential developed for Tenax GC (35/60) cartridge with an i.d. of 1.056 cm during vacuum sampling.

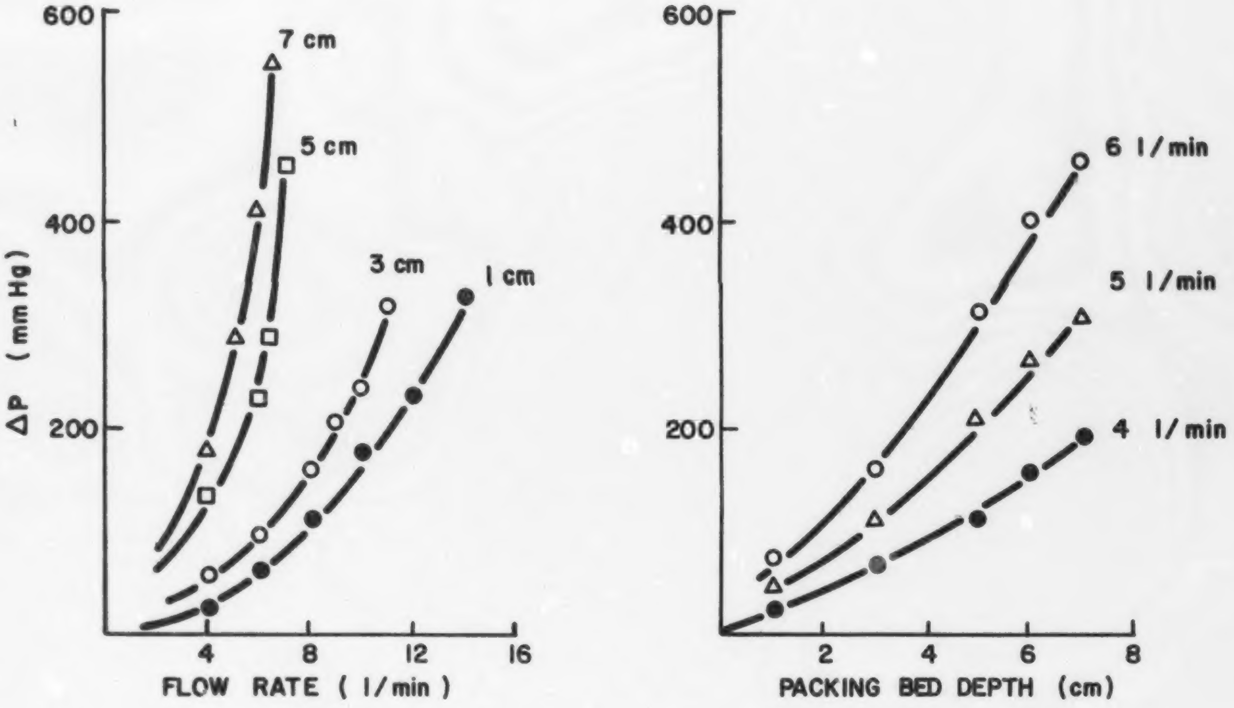


Figure 24. Pressure differential for Chromosorb 101 (60/80) for air drawn through a 1.056 cm i.d. cartridge.

Experimental

To determine ET and EV a dual tandem cartridge arrangement and the sampling system described in Section VIII were used. At the beginning of each sampling period a known quantity of vapor (methyl ethyl ketone, phenyl methyl ether and/or nitrobenzene) was introduced directly into the entrance corridor of the front cartridge. Periodically (15 and 30 min intervals) the back cartridge was replaced with a virgin one and the backup cartridge was examined by thermal desorption-glc (Section VII). At the end of the experiment the front cartridge of the duo-series was also analyzed. Peak areas for each standard were calculated to determine the amount of vapor disappearing from the front cartridge and appearing in the second, backup cartridge. The ET and EV values of four unidentified constituents (to be identified by glc-ms) present in ambient air were also determined.

Breakthrough on total "pollutant profile" was also evaluated by using the duo-tandem cartridge arrangement. The area under the chromatographic peaks developed from a glc program run (75-165°C, 10°/min, 12 ft 2% DEGS column) for each cartridge was estimated with a planimeter and expressed as a percent of the total area for each set of tandem cartridges.

Results and Discussion

Table 9 presents the results observed for packing bed dimensions of 1.056 cm i.d. x 1 cm in length (front and back). No methyl ethyl ketone (MEK) or nitrobenzene (NB) could be detected in either the front or backup cartridge at any time during sampling. On the basis of these observations it was concluded that breakthrough (and possible low collection efficiencies) had occurred in less than 15 min. On the otherhand P1, P2, P3 and P4 was detected and appeared to remain relatively constant in the backup cartridge throughout the entire sampling period. Since P1-P4 were endogenous interfering

Table 9. ELUTION VOLUME CHARACTERISTICS FOR TENAX GC (35/60)[a] - 1 CM BED DEPTH

Sampling Time (Min)	Volume Air Sampled (1)	Peak Area (Cm^2)[b]					
		MEK	P1	P2	P3	P4	NB
15	180	ND[c]	1.7	1.9	2.7	1.9	ND
45	540	ND	1.8	1.9	1.9	0.7	ND
75	900	ND	2.2	2.5	3.0	1.0	ND
105	1260	ND	1.9	4.0	6.5	1.9	ND
165	1980	ND	3.0	4.1	4.8	2.6	ND
195	2340	ND	1.9	3.4	3.7	1.8	ND
225	2700	ND	2.0	1.9	4.0	2.2	4.3
255	3060	2.8	2.7	1.6	3.7	2.2	ND
315	3780	ND	-	-	-	-	ND
Front Cartridge		ND	9.2	11.5	13.5	10.0	ND

[a] Packing bed Dimensions - Front Cartridge: 1 cm dia. x 1 cm in length.
Backup Cartridge: identical to front sampler.
Sampling rate - 12 l/min; sampling location - Res. Tri. Prk.

[b] P1, P2, P3, P4 are unidentified peaks appearing at 100, 115, 135, and 165°C, respectively in chromatogram of air sample.

[c] ND = not detected.

constituents in ambient air and were probably present during the entire sampling period (frontal analysis), it could not be concluded whether these results reflected low collection efficiencies, early breakthrough or both.

Because early breakthrough was suspect in the previous experiment, another study was conducted which utilized a 1.056 i.d. x 1 cm long and a 1.056 x 3 cm long front and back cartridges, respectively. Table 10 shows these results. In this case early breakthrough for MEK and NB was

Table 10. ELUTION VOLUME CHARACTERISTICS FOR TENAX GC (35/60)[a] - 1 AND 3 CM BED DEPTHS

Sampling Time (Min)	Volume Air Sampled (1)	Peak Area (Cm^2)[b]					
		MEK	P1	P2	P3	P4	NB
15	180	ND[c]	1.8	5.3	7.3	2.5	12
30	360	6.6	1.6	3.7	4.8	1.5	13
60	720	ND	2.6	2.7	5.3	2.0	14
90	1080	ND	2.6	5.3	6.3	1.4	19
120	1440	[d]1.2	3.2	5.1	8.0	2.7	25
150	1880	2.0	3.0	6.3	8.5	3.1	26
180	2160	ND	-	-	-	-	30
210	2560	ND	-	-	-	-	24
240	2880	ND	-	-	-	-	20
Front Cartridge		ND	4.9	6.0	5.4	26.0	2.5

[a] Packing bed dimensions - Front Cartridge: 1 cm dia. x 1 cm in length
Backup Cartridge: 1 cm dia. x 3 cm in length
Sampling rate - 12 l/min; sampling location - Res. Tri. Prk.

[b] See Table 1 for description of P1, P2, etc.

[c] ND = not detected.

[d] May be a contaminant peak.

detected which is consistent with the previous conclusions. Since the air sample was drawn through the cartridge, a vacuum gradient was created across the packing bed. This situation probably leads to vacuum desorption or "stripping" of the analyte and therefore early breakthrough of solute vapors. In effect a smaller EV occurs for the backup cartridge than for the front cartridge (the pressure differential across increasing packing bed lengths are shown to be nonlinear).

Tables 11 and 12 present EV characteristics for packing bed lengths of 2 and 3 cm. Breakthrough occurred after approximately 1.5 m^3 of air

Table 11. ELUTION VOLUME CHARACTERISTICS FOR TENAX GC (35/60)[a] - 2 CM BED DEPTH

Sampling Time (Min)	Volume Air Sampled (1)	Peak Area (Cm^2)[b]				
		P1	P2	P3	P4	NB
15	180	2.0	0.8	3.0	2.2	ND[c]
45	540	2.9	3.1	5.1	1.9	ND
75	900	2.2	1.6	6.6	1.6	ND
105	1260	2.6	3.3	4.0	1.4	ND
135	1620	4.8	5.2	8.4	3.5	75.6
165	1980	3.9	3.6	6.6	2.8	47.2
195	2340	3.7	3.2	8.2	3.3	40.0
225	2700	2.4	6.5	7.9	3.2	40.0
255	3060	4.7	6.0	9.6	5.0	35.0

[a] Packing bed dimensions - Front Cartridge: 1 cm dia. x 2 cm in length
Backup Cartridge: same as above
Sampling rate - 12 l/min; sampling location - Res. Tri. Prk.

[b] P1, P2, P3, P4 are described in Table 6.

[c] ND = not detected

was sampled for a 2 cm bed length of sorbent. Increasing the bed depth to 3 cm prevented breakthrough; all of the NB was detected in the front cartridge. The EV for MEK was about 2 M^3 for a 1 x 3 cm cartridge.

Two sampling rates 12 and 24 l/min were compared to determine whether the elution volume characteristics were flow dependent. The results shown in Tables 13 and 14 indicated that breakthrough is relatively independent of sampling rate when phenyl methyl ether (PME) and nitrobenzene (NB) were used as the test vapors. Analysis of the front cartridge revealed the presence of PME and NB and therefore breakthrough had not occurred.

Table 12. ELUTION VOLUME CHARACTERISTICS FOR TENAX GC (35/60)[a] - 3 CM BED DEPTH

Sampling Time (Min)	Volume Air Sampled (1)	Peak Area (Cm^2)[b]					
		MEK	P1	P2	P3	P4	NB
15	180	ND[c]	1.8	2.5	2.6	1.2	ND
45	540	ND	1.2	2.4	1.4	0.8	ND
75	900	ND	1.6	2.2	3.7	1.3	ND
105	1260	ND	1.5	4.2	7.6	1.5	ND
135	1620	ND	1.7	4.5	4.3	1.9	ND
165	1980	18.0	1.7	3.8	5.0	1.9	ND
195	2340	25.0	1.6	3.9	5.4	1.8	ND
225	2700	15.0	0.8	3.4	4.0	1.5	ND
255	3060	ND	1.0	3.7	4.7	2.2	ND
Front Cartridge		ND	9.6	11.5	20.4	5.7	8.4

[a] Packing bed dimensions - Front Cartridge: 1 cm dia. x 3 cm in length
Backup Cartridge: same as above
Sampling rate - 12 1/min; sampling location - Res. Tri. Prk.

[b] See Table 6 for description of P1, P2, etc.

[c] ND = not detected

Using a flow of 24 1/min, 4 cm and 6 cm beds of Tenax GC (35/60) were evaluated and breakthrough did not occur for NB even after 15 m^3 of air had been drawn through the front cartridge and analysis of the front cartridge by glc confirmed the presence of NB (Tables 15 and 16). On the otherhand, PME appeared to breakthrough after about 9 m^3 of air had been sampled through a 6 cm bed of Tenax GC packing but not for a 4 cm bed. This was attributed to the higher vacuum experienced with a 6 cm bed to maintain a 24 1/min flow rate and thus "vacuum stripping" of PME probably occurred.

Table 13. ELUTION VOLUME CHARACTERISTICS FOR TENAX GC (35/60)[a] - 2 CM BED DEPTH AND 12 L/MIN

Sampling Time (Min)	Volume Air Sampled (1)	Peak Area (Cm^2)[b]						
		P1	PME	P2	P3	P4	P5	NB
15	170	1.3	ND	1.9	4.1	1.9	0.9	ND[c]
30	350	1.3	ND	1.9	5.5	1.5	0.6	ND
60	710	3.2	ND	2.3	2.1	1.5	0.6	ND
90	1060	3.1	ND	4.9	10.5	3.6	1.3	ND
120	1420	2.5	ND	4.1	11.0	5.6	2.8	ND
150	1770	3.2	ND	3.0	3.8	3.0	1.8	ND
180	2120	3.4	ND	2.9	3.0	3.3	1.8	ND
210	2480	1.9	ND	0.8	1.8	0.9	0.9	ND
240	2830	1.2	ND	1.1	1.6	1.1	1.0	ND
270	3190	1.4	ND	2.6	6.8	3.7	1.7	ND
Front Cartridge	3190	3.6	7.2	6.4	12.6	30.0	9.6	10.8

[a] Packing bed - Front Cartridge: 1.5 cm i.d. x 2.0 cm in length.
Backup Cartridge: 1.5 cm i.d. x 3.0 cm in length.
Sampling rate - 12 l/min; sampling location - Res. Tri. Prk.

[b] P1, P2, P3, P4, P5 were peaks eluting at 81°, 95°, 110°, 135°, and 165°, respectively; see text for glc conditions.

[c] ND = not detected

A comparison of the "pollutant profile" from Los Angeles, CA. for the front and backup cartridges were also made to evaluate overall breakthrough for Tenax GC and Chromosorb 101 sorbents during field sampling. These results are given in Table 17. Early breakthrough from the front cartridge resulted when Chromosorb 101 was used as the collection media. In contrast, more than 90% of the "profile" collected on Tenax GC was still in the front cartridge after 5.6 m^3 of air had been sampled.

Table 14. ELUTION VOLUME CHARACTERISTICS FOR TENAX GC (35/60)[a] - 2 CM BED DEPTH AND 24 L/MIN

Sampling Time (Min)	Volume Air Sampled (l)	Peak Area (cm^2)[b]						
		P1	PME	P2	P3	P4	P5	NB
15	350	1.1	ND	2.0	3.4	2.1	1.1	ND[c]
30	710	1.7	ND	2.8	7.2	3.1	1.1	ND
60	1420	2.4	ND	3.8	8.8	4.9	1.9	ND
90	2120	1.4	ND	2.4	4.4	4.8	2.0	ND
150	3540	1.2	ND	2.1	5.7	4.5	1.6	ND
180	4250	2.5	ND	3.4	10.0	2.1	0.9	ND
Front Cartridge	4250	1.5	13.0	4.6	8.8	9.6	5.0	3.4

[a] Packing bed - Front Cartridge: 1.5 cm i.d. x 2.0 cm in length
Backup Cartridge: 1.5 cm i.d. x 3.0 cm in length
Sampling rate - 24 l/min; sampling location - Res. Tri. Prk.

[b] P1, P2, P3, P4, P5 were unidentified peaks eluting at 30°, 95°, 110°, 135°, and 165°, respectively; see text for glc conditions.

[c] ND = not detected

Table 15. ELUTION VOLUME CHARACTERISTICS FOR TENAX GC (35/60)[a]- 4 CM BED DEPTH

Sampling Time (min)	Volume Air Sampled (1)	Peak Area (cm^2)[b]						
		P1	PME	P2	P3	P4	P5	NB
30	710	2.0	ND	2.4	5.8	4.5	1.3	ND[c]
60	1420	1.7	ND	1.3	2.1	1.3	0.7	ND
90	2120	2.6	ND	3.7	7.0	4.3	2.8	ND
120	2830	0.8	ND	1.4	3.1	1.8	0.5	ND
150	3540	3.8	ND	4.5	7.7	4.5	1.5	ND
180	4250	2.9	ND	3.4	7.5	8.5	3.7	ND
210	4960	2.8	ND	4.5	10.5	14.0	3.8	ND
240	5660	3.4	ND	3.3	7.0	2.8	1.8	ND
270	6370	1.2	ND	1.0	2.4	1.6	0.7	ND
300	7080	3.5	ND	4.5	10.5	8.1	3.5	ND
330	7790	2.1	ND	2.4	5.2	2.6	1.3	ND
360	8500	2.0	ND	2.6	5.2	5.5	2.4	ND
390	9200	2.9	ND	3.1	7.5	9.1	4.0	ND
420	9910	2.0	ND	2.8	7.6	10.5	3.6	ND
450	10620	2.1	ND	3.2	6.7	9.0	4.3	ND
480	11330	2.8	ND	3.3	8.5	5.4	2.1	ND
Front Cartridge	11330	1.6	7.4	2.0	4.6	5.8	4.8	3.4

[a] Packing bed - Front Cartridge: 1.5 cm i.d. x 4 cm in length
Back Cartridge: 1.5 cm i.d. x 3 cm in length
Sampling rate - 24 1/min; location - Res. Tri. Prk.

[b] See previous Table for explanation of P1, P2, etc.

[c] ND = not detected.

Table 16. ELUTION VOLUME CHARACTERISTICS FOR TENAX GC (35/60)[a] - 6 CM BED DEPTH

Sampling Time (min)	Volume Air Sampled (1)	Peak Areas (cm^2)[b]						
		P1	PME	P2	P3	P4	P5	NB
30	350	0.84	ND	2.5	4.1	2.3	0.4	ND[c]
60	710	0.68	ND	1.5	2.8	4.6	0.7	ND
90	1060	0.50	ND	1.4	1.9	1.5	0.4	ND
150	1770	1.40	ND	2.9	4.5	2.4	0.6	ND
210	2480	1.68	ND	3.0	5.4	1.9	0.6	ND
270	3190	2.64	ND	4.9	5.5	2.8	0.6	ND
300	3540	0.55	ND	0.9	2.0	1.8	0.6	ND
330	3890	1.35	ND	0.9	2.0	0.9	0.6	ND
360	4250	1.20	ND	1.2	2.3	3.6	1.3	ND
390	4600	2.40	ND	1.9	5.5	2.6	1.0	ND
420	4960	3.38	ND	1.5	3.8	1.7	0.8	ND
480	5660	-	ND	4.8	10.5	6.3	2.2	ND
540	6370	-	ND	1.2	3.1	1.1	1.0	ND
570	6730	-	ND	2.1	6.5	3.7	0.8	ND
600	7080	-	ND	3.2	9.3	7.2	2.4	ND
660	7790	-	ND	2.2	4.8	1.8	1.5	ND
720	8500	-	ND	1.7	4.9	2.2	1.5	ND
750	8850	2.53	10.8	1.0	2.3	1.9	1.0	ND
810	9560	3.00	3.0	3.1	8.4	5.2	1.7	ND
870	10270	3.18	ND	3.2	8.2	7.5	2.6	ND
930	10970	1.62	ND	1.7	4.5	4.7	1.7	ND
960	11330	3.00	ND	3.0	6.2	6.8	3.5	ND

Table 16 (continued). ELUTION VOLUME CHARACTERISTICS FOR TENAX GC (35/60)[a] - 6 CM BED DEPTH

Sampling Time (min)	Volume Air Sampled (l)	Peak Areas (cm^2)[b]						
		P1	PME	P2	P3	P4	P5	NB
1020	12040	2.40	ND	2.0	4.1	2.5	3.0	ND[c]
1080	12740	1.75	ND	2.4	3.8	6.0	3.2	ND
1140	13450	1.75	ND	2.2	4.9	8.2	2.8	ND
1200	14160	0.84	ND	1.7	4.0	2.1	2.0	ND
1260	15000	1.00	ND	-	-	-	-	ND
Front Cartridge	15000	1.20	ND	-	-	-	-	4.8

[a] Packing bed - Front Cartridge: 1.5 cm i.d. x 6 cm in length
Back Cartridge: 1.5 cm i.d. x 3 cm in length
Sampling rate - 24 l/min; location - Res. Tri. Prk.

[b] See Table 14 for explanation of P1, P2, etc.

[c] ND = not detected

Table 17. POLLUTANT PROFILE BREAKTHROUGH DURING AMBIENT AIR SAMPLING[a]

Sorbent	Cartridge Dimensions	Sampling Time (Min)	Volume Air Sampled (1)	Percent of Combined Area[b]
Chromosorb 101 (60/80)				
	Front 1.5 x 3.0 cm	30	450	75
	Backup 1.5 x 3.0 cm	30	450	25
	Front 1.5 x 3.0 cm	60	1340	40
	Backup 1.5 x 3.0 cm	60	1340	60
	Front 1.5 x 3.0 cm	90	3970	40
	Backup 1.5 x 3.0 cm	90	3970	60

	Front 1.5 x 1.5 cm	30	400	90
	Backup 1.5 x 1.5 cm	30	400	10
	Front 1.5 x 1.5 cm	60	1400	55
	Backup 1.5 x 1.5 cm	60	1400	45
	Front 1.5 x 1.5 cm	120	5400	40
	Backup 1.5 x 1.5 cm	120	5400	60

Tenax GC (35/60)				
	Front 1.5 x 3.0 cm	60	1260	90
	Backup 1.5 x 3.0 cm	60	1260	10
	Front 1.5 x 3.0 cm	120	5600	95
	Backup 1.5 x 3.0 cm	120	5600	5

---

[a] Experiments were performed in Santa Monica, CA.

[b] The total area of the chromatogram between 75-160° (10°/min) on a 12 ft 2% DEGS column was determined using a planimeter.

SECTION VI

GAS CHROMATOGRAPHIC INLET-MANIFOLD FOR SAMPLE ANALYSIS

Because of the limited sensitivity of currently available detectors hazardous substances need to be concentrated from highly dilute samples. A step toward the solution of this problem is achieved when cartridges containing an appropriate sorbent is used and large volumes of air are forced or drawn through the sampling device whereupon the pollutants are trapped. The performance (collection efficiency, pressure differential, elution volume) characteristics for a selected number of sorbents was described in Section V.

Even when employing a cartridge technique, only trace quantities of hazardous pollutants are accumulated; thus, it is imperative that the entire sample be submitted for analysis. The levels of carcinogenic and mutagenic vapors (e.g. epoxides, nitrosamines, sulfonates, sulfites, sultones, aldehydes, ketones, β-lactones, chloroalkyl ethers and nitro compounds) to be collected and identified from ambient air under this research program are anticipated to occur at ng/m^3 amounts or less. These severe restrictions on sampling and analysis have required the development of a technique(s) such as thermal desorption as a means of transferring the entire amount of trapped vapors from the cartridge to the analytical system.

This section describes (1) the design and fabrication of an inlet-manifold for effecting desorption of vapors and efficient transfer of pollutants to a glc, and (2) the heating characteristics of selected sorbents using the inlet-manifold.

DESIGN AND FABRICATION OF INLET-MANIFOLD

Thermal desorption systems of varying designs have been described[16-21,28,45-7] for recovering trapped vapors and their subsequent analysis by glc and glc-ms. Duel's[46] solvent-free sample inlet system was designed so that with the sample fraction "in-line" with the sample, the entire mixture could be introduced directly onto the glc column. This concept was retained for the development in this research program of an interface system for analyzing carcinogenic vapor samples by glc and glc-ms.

The described manifold design evolved from a consideration of several criteria. These were: (1) the heat transfer characteristics of cartridge samplers containing sorbents of various physical dimensions, (2) the flow rate requirements for purging desorbed vapors from the cartridge sampler and for packed and glc capillary columns, (3) the temperatures necessary for effecting thermal desorption of trapped carcinogenic vapors from sorbents (from Section VII), and (4) the ability to conveniently interchange and assemble on any standard glc or glc-ms instrument.

The fabricated inlet/manifold system (Fig. 25) consisted of four main components: a desorption chamber, a six-port two position high temperature low volume valve (Valco Inc., Houston, Tx.), a Ni capillary trap, and a temperature controller. One of the three prototype brass thermal desorption chambers constructed for use in this program is shown in Figure 26. Brass was chosen for its good conductive properties. The configuration of the chamber was designed to allow an inert gas to enter through a sidearm near the bottom and sweep up an annular space between the chamber and glass cartridge. This permitted the purge gas to be preheated to the chamber temperature prior to passing down through the sorbent bed. Two additional prototype brass desorption chambers were designed so that the purge gas entered near the top and passed directly through the glass cartridge to the valve proper (Fig. 27). The overall chamber lengths were

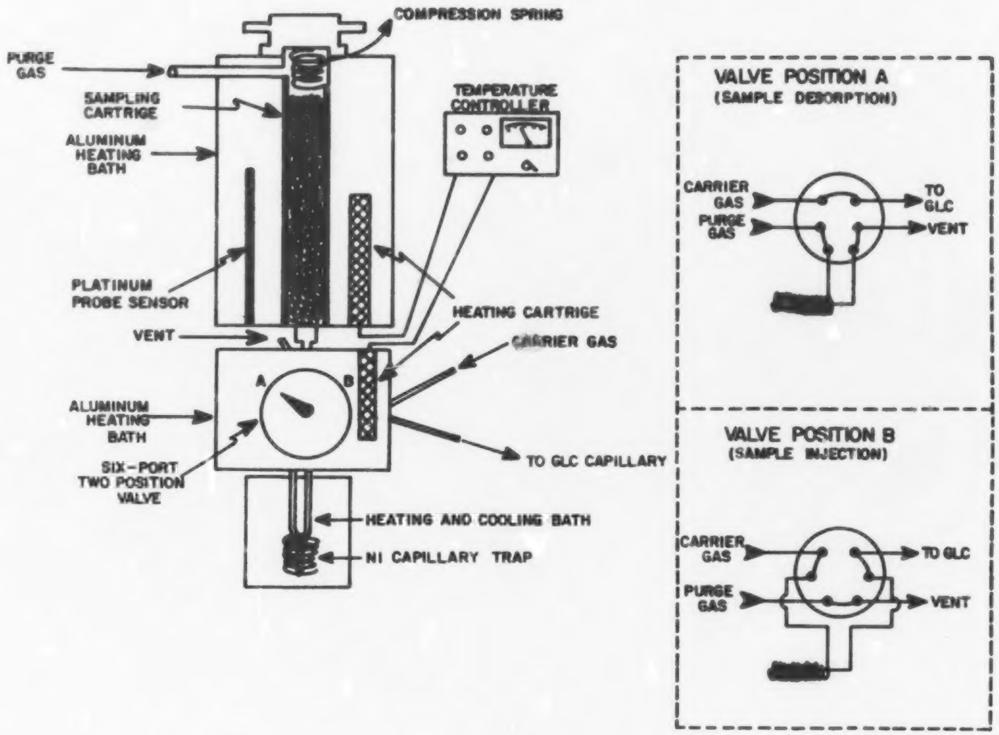

COMPRESSION SPRING
PURGE GAS
SAMPLING CARTRIGE
ALUMINUM HEATING BATH
TEMPERATURE CONTROLLER
PLATINUM PROBE SENSOR
HEATING CARTRIGE
VENT
CARRIER GAS
A
B
ALUMINUM HEATING BATH
SIX-PORT TWO POSITION VALVE
TO GLC CAPILLARY
HEATING AND COOLING BATH
NI CAPILLARY TRAP
VALVE POSITION A
(SAMPLE DESORPTION)
CARRIER GAS
PURGE GAS
TO GLC
VENT
VALVE POSITION B
(SAMPLE INJECTION)
CARRIER GAS
PURGE GAS
TO GLC
VENT

Figure 25. Thermal desorption inlet-manifold

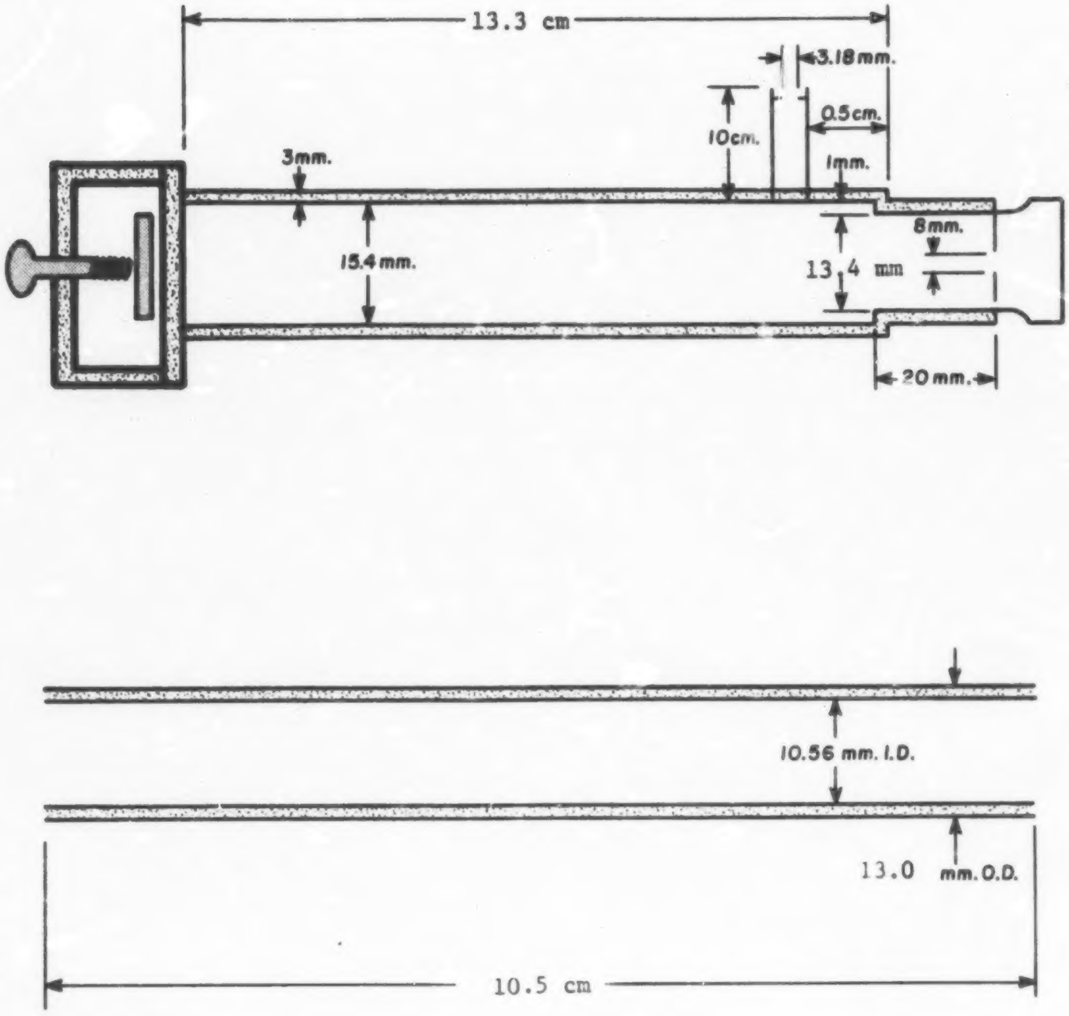

13.3 cm
3.18mm.
10cm.
0.5cm.
3mm.
1mm.
15.4mm.
8mm.
13.4 mm
20mm.
10.56 mm. I.D.
13.0 mm. O.D.
10.5 cm

Figure 26. Thermal desorption chamber with annular space. Sampling tube shown in lower figure.

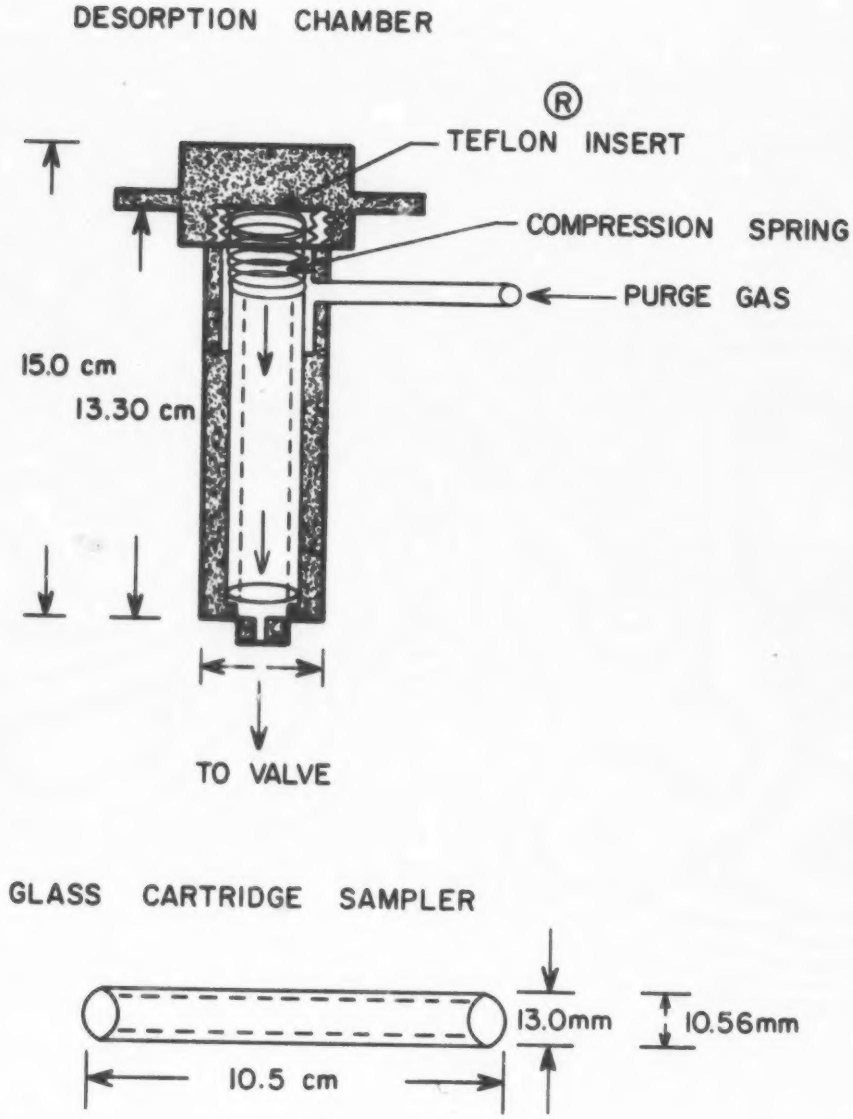

DESORPTION CHAMBER
®
TEFLON INSERT
COMPRESSION SPRING
PURGE GAS
15.0 cm
13.30 cm
TO VALVE
GLASS CARTRIDGE SAMPLER
13.0mm
10.56mm
10.5 cm

Figure 27. Thermal desorption chamber

13.3 cm which accommodated a pyrex sampling cartridge 10.5 cm in length. Two of the desorption chambers (Fig. 20 and 21) were designed to accept cartridges 10.56 mm i.d. x 13.0 mm o.d. While the third accepted a larger cartridge of 15.6 mm i.d. x 16.5 mm o.d.

An aluminum sandwich served as a heat sink (Fig. 25) which accepted any one of the three desorption chambers. Two 150 w, 115V heating cartridges (Varian Part No. 22-0000-18-00) were used to heat the aluminum sandwich and the temperature was monitored and controlled with a platinum sensor probe (100Ω, Varian Part No. 64-000009). The desorbed vapors passed via a short insulated capillary line through a six-port two position valve which was also encased in an aluminum heating bath. Temperature control was identical [illegible] thermal desorption chamber. The electronics circuit which controlled the temperatures on each heat sink is shown in Figure 28. The temperature was monitored directly on a pyrometer; control was ± 1°C.

A nickel capillary (0.020 i.d. x 0.032 x 0.5 m in length) constituted one loop of the valve proper which was cooled with liquid N_2 or solid carbon dioxide/isopropanol and served as a trap for collecting and concentrating desorbed vapors for their introduction into high resolution glc columns. The vapors were released from the capillary trap by rapidly heating to 175° using a wax bath.

The multiport valve used on the described inlet/manifold was chosen for its polyimide internal stem to minimize the contact of desorbed trace vapors with reactive metal surfaces, therefore, mimimizing contamination or decomposition of sample constituents.

In a typical thermal desorption cycle a sampling cartridge was placed in the preheated (ca. 225°C) chamber, and N_2 gas was purged through the cartridge (ca. 20 ml/min) to purge the vapors into the liquid N_2 cooled

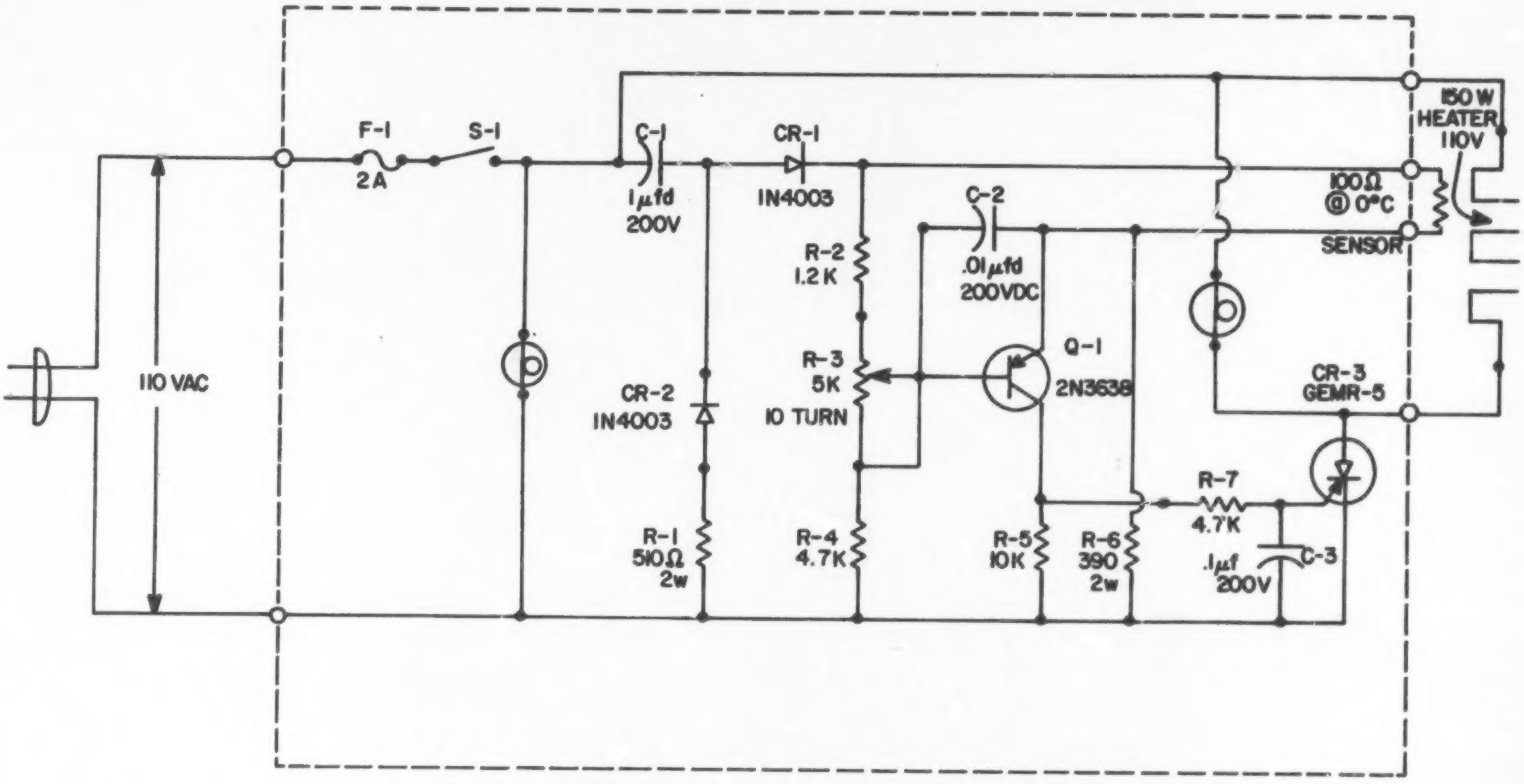

F-1
2A
S-1
C-1
1 μfd
200V
CR-1
IN4003
C-2
.01 μfd
200VDC
100 Ω
@ 0°C
SENSOR
150 W
HEATER
110V
110 VAC
R-2
1.2 K
R-3
5K
10 TURN
Q-1
2N3638
CR-2
IN4003
CR-3
GEMR-5
R-1
510 Ω
2w
R-4
4.7K
R-5
10K
R-6
390
2w
R-7
4.7K
.1 μf
200V
C-3

Figure 28. Electronics circuit designed for temperature control on inlet-manifold system.

Ni capillary trap; this constituted valve position "A" (Fig. 25). After the thermal desorption step was complete, the six-port valve was rotated to position "B" (Fig. 25) and the temperature on the capillary loop was rapidly raised (> 10°/min) whereupon the carrier gas carried the vapors onto a glc column.

As designed, the prototype thermal desorption chambers which were easily interchangeable, accommodated cartridges of two different diameters with up to 8 cm of packing (sorbent) depth. Thus, comparisons of different cartridge sizes with respect to sorbent background during thermal desorption could be made. This inlet-manifold configuration also allowed the desorbed vapors from one or more cartridges to be accumulated in the capillary trap prior to analysis by glc or glc-ms.

The inlet/manifold system described here was employed in studies on thermal desorption of vapors from cartridges. Its performance characteristics are further discussed in Section VII.

HEAT TRANSFER CHARACTERISTICS FOR SELECTED SORBENTS AND THERMAL DESORPTION CHAMBER

An investigation was made of the heating rates for candidate sorbent media. Using the measured heat transfer coefficients as a guideline, the required heating period and temperature for effecting quantitative desorption was selected (Section VII). Furthermore, two prototype desorption chamber designs with and without an annular space (Fig. 26 and 27) were compared with regard to the rate of heat transfer to the sorbent bed.

Experimental

Tenax-GC (60/80 mesh), Chromosorb 101 (100/120), Chromosorb 104 (100/120) and Chromosorb W-HP (100/120) were purchased from Applied Science, State College, Pa. Stationary phases chemically bonded to supports which included carbowax 400/Poracil C (100/120) and oxopropionitrile/Poracil C (80/100) were also obtained from Applied Science. Carbowax 600 and didecyl phthalate stationary phases and the sorbent Porapak Q were from Supelco, Inc., Bellefonte, Pa.

Carbon derived from coke (PCB, 12/30) was acquired from Pittsburgh Activated Carbon Division of Calgon Corp., Pittsburgh, Pa. A cocoanut activated carbon (580-26) was purchased from Barneby Cheney, Columbus, Ohio.

The temperature rise times in the sorbent bed of the cartridge was measured with a calibrated thermocouple (mV vs °C); signal output was directly recorded on a strip chart recorder (Varian Model A-25, Varian Instruments, Walnut Creek, CA.). The rate of temperature increase in the sorbent was determined using preset and isothermal desorption chamber temperatures. The rate of temperature increase was also monitored on the inner glass wall of the cartridge.

Results and Discussion

Prior to defining the parameters (temperature, heating time) for effecting thermal desorption of vapors trapped on sorbents (Section VII), the rate of heat transfer from the thermal sink to the sorbent bed was measured using the inlet-manifold interface depicted in Figure 25. Operating the desorption unit under isothermal conditions, the temperature increase in the sorbent bed was monitored immediately after inserting a cartridge.

Figure 29 depicts the thermocouple response time, and the heating rate in the center of a cartridge containing Tenax GC using one of the previously described thermal desorption chambers (Fig. 27). Because the response of the thermocouple significantly contributed to the temperature rise profile (8 sec required to reach 63% of the upper temperature limit), its contribution

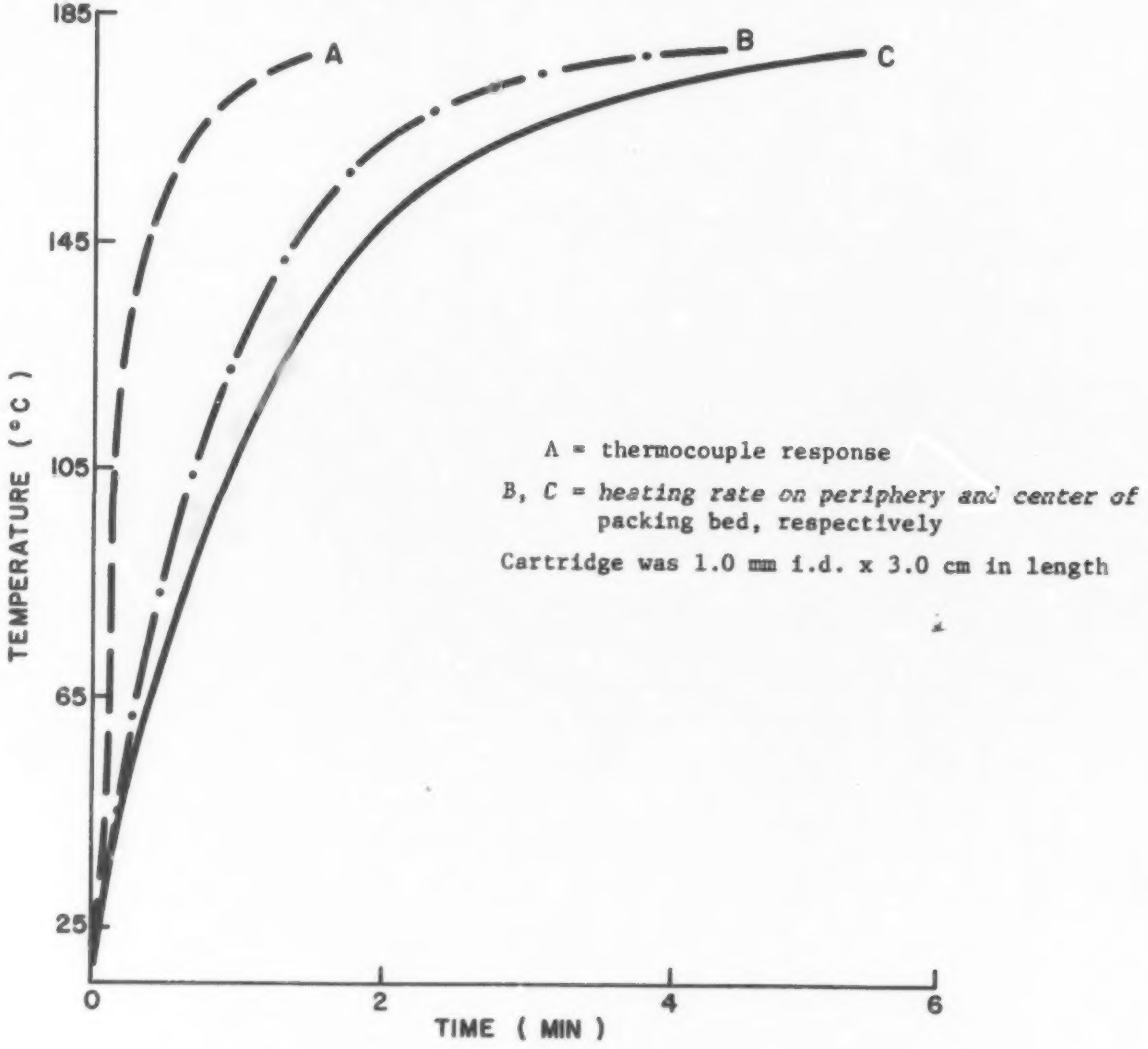


Figure 29. Differential heating rate in a glass cartridge containing Tenax GC (60/80).

was subtracted from all measurements. These temperature rise times (Fig. 29) indicated a cross-sectional gradient was produced immediately after inserting the cartridge into the chamber. The periphery of the sorbent bed reached the temperature maximum in approximately 4 min, while the center of the sorbent bed required an additional 2 min. Furthermore increasing the cartridge diameter from 1.0 to 1.5 cm increased the temperature differential by a factor of 1.3.

The heat transfer coefficient for sorbents and similarly their observed differential temperature gradient, varied considerably. The relative temperature rise times for several sorbents which previously were shown to have good collection efficiencies (Section V) were compared. The order of their heating rates were observed to be: PCB and BPL carbon (12 x 30) > oxopropionitrile and carbowax 400 chemically bonded to Poracil C (100/120) > Chromosorb 104 (100/120) > Tenax GC (60/80) and Chromosorb 101 (100/120). These results are depicted in Figure 30 which were obtained with a thermal desorption chamber designed to have an annular space between the chamber wall and glass cartridge. The largest differences in heating rates (in the center of the sorbent bed) were exemplified by the activated carbons and Tenax GC (Fig. 30).

Because inspection of the heating rates for Tenax GC (60/80) with and without an annular space indicated relative differences (Fig. 29 and 30), a more detailed study was conducted comparing these two thermal desorption chamber designs. Figure 31 presents this comparison. This data clearly shows that a 1 mm annular space in the chamber reduced the heating rate of the inner glass cartridge wall as well as the center of the packing by at least a factor of two. Furthermore, a larger heating gradient was observed between the center and periphery of the sorbent bed with the annular spaced

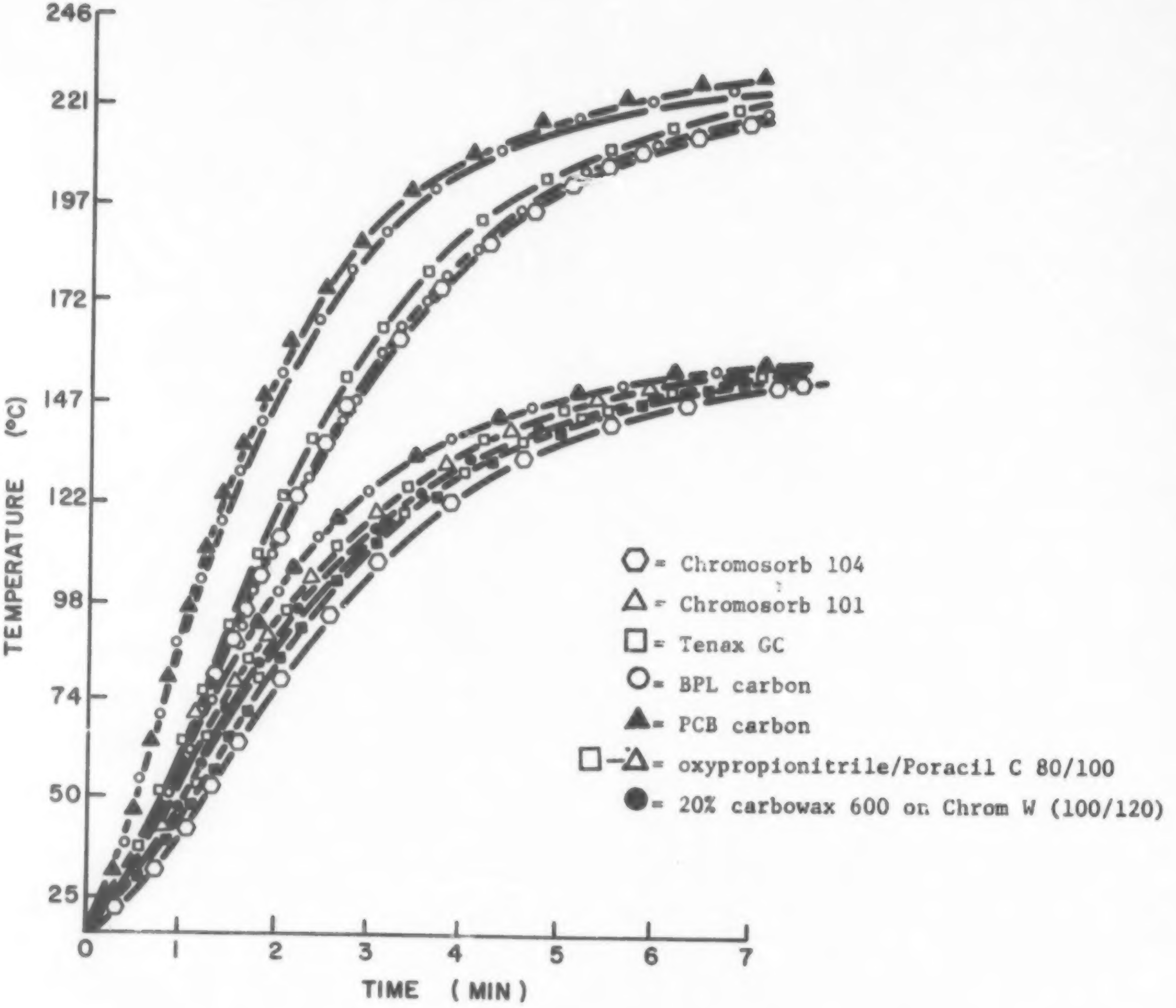


Figure 30. Temperature rise times in sorbent bed using annular spaced chamber.

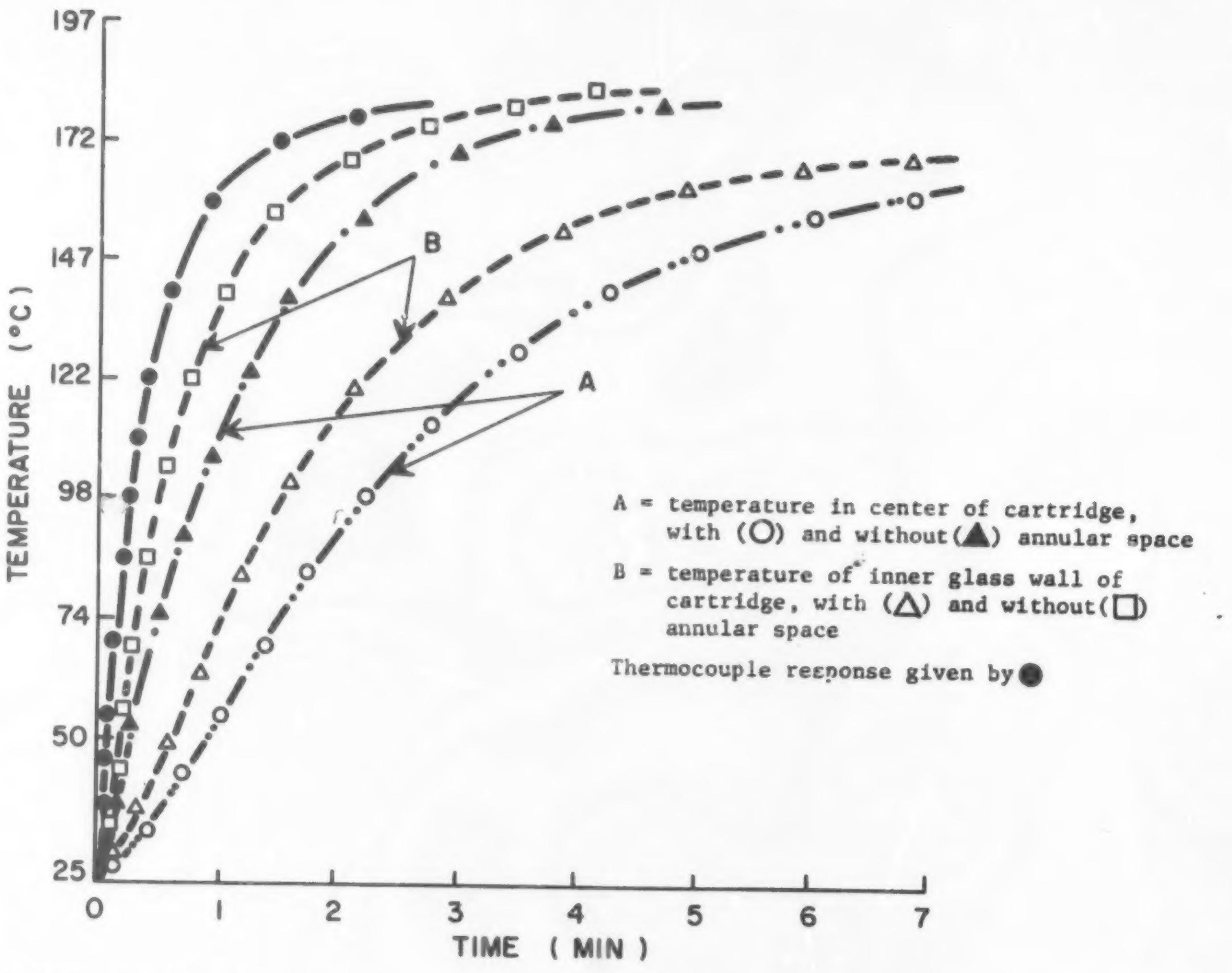


Figure 31. Comparison of temperature rise times for chambers with and without an annular space. Chamber was at 175°C.

chamber than the one providing direct contact between the brass wall and glass cartridge.

In view of the results obtained with the prototype desorption chamber with an annular space (Fig. 26), the heating rates for candidate sorbent media were also investigated with a chamber providing direct contact between the glass cartridge and chamber wall (Fig. 27). In general the trend was the same as previously observed (compare Fig. 30 and 32) except all heating rates were significantly greater in this case.

Since the heating rate was generally 1.7 times faster when the cartridge was in direct contact with the brass desorption chamber wall and a smaller temperature gradient was observed through the packing bed, it was concluded that a chamber incorporating a 1 mm annular space 90% of the length of the cartridge was not a feasible design for application to desorption of vapors. Thus, the prototype desorption chamber which introduced the carrier gas near the top of the chamber (Fig. 27) was employed in thermal desorption of vapors trapped on sorbents.

The temperature rise time for Tenax GC was also examined using three isothermal conditions on the desorption unit (Fig. 33). The heating rate (slope) was only slightly increased by increasing the desorption unit temperature; however, it was evident that the rate was linear upto 65% of the final temperature or during the first 75 sec. Thereafter, an additional several minutes was required to reach a plateau. These data, therefore, indicate that the desorption unit should be set at a temperature which allows the attainment of the required desorption temperature in 60-90 sec after insertion of the cartridge sampler.

When a thermal desorption chamber design permits rapid heating of the cartridge sampler with a minimum of temperature gradient across the packing

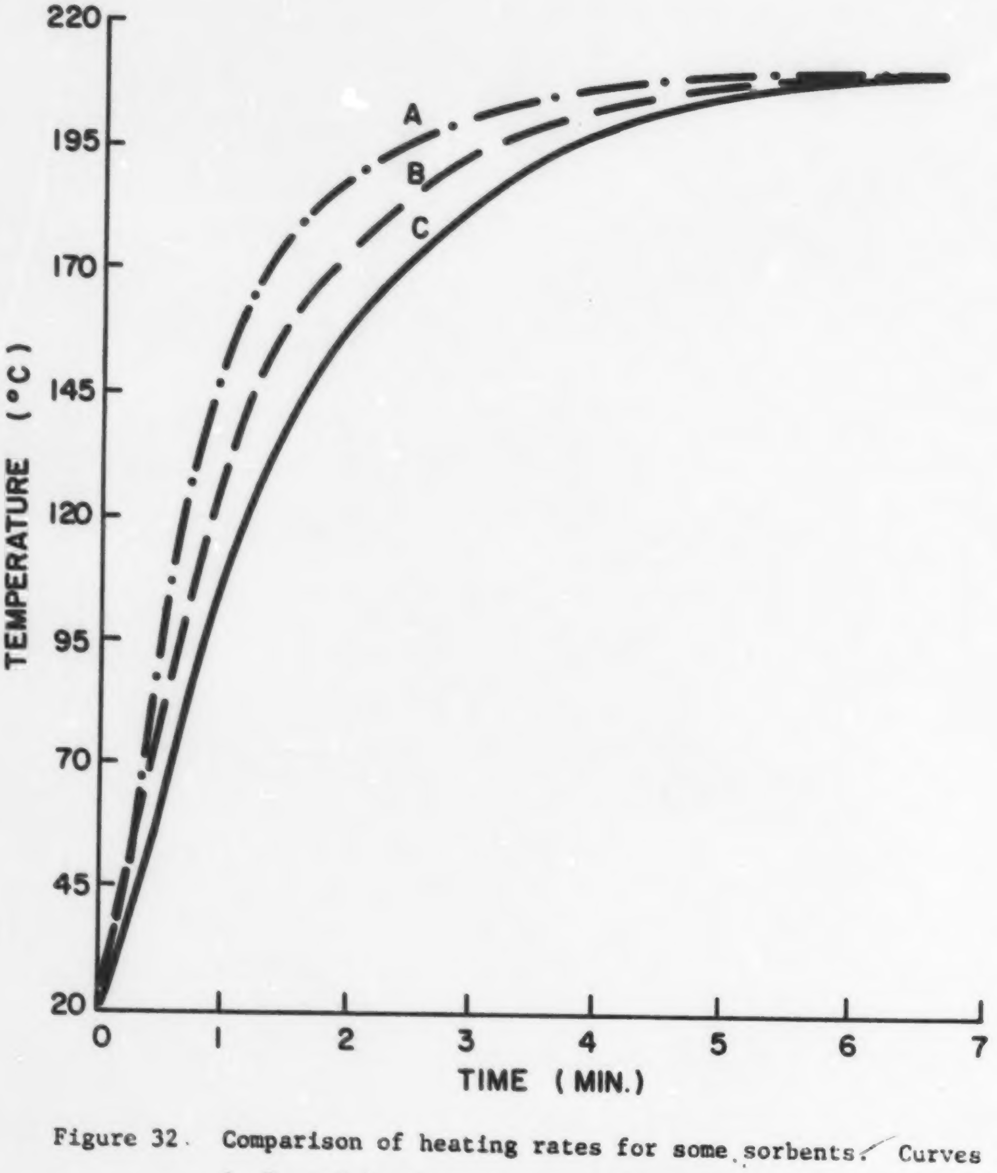


Figure 32. Comparison of heating rates for some sorbents. Curves A, B, and C correspond to PCB carbon (12/30), oxopropionitrile on Poracil C (80/100), respectively. Thermal desorption chamber was isothermal at 210°C.

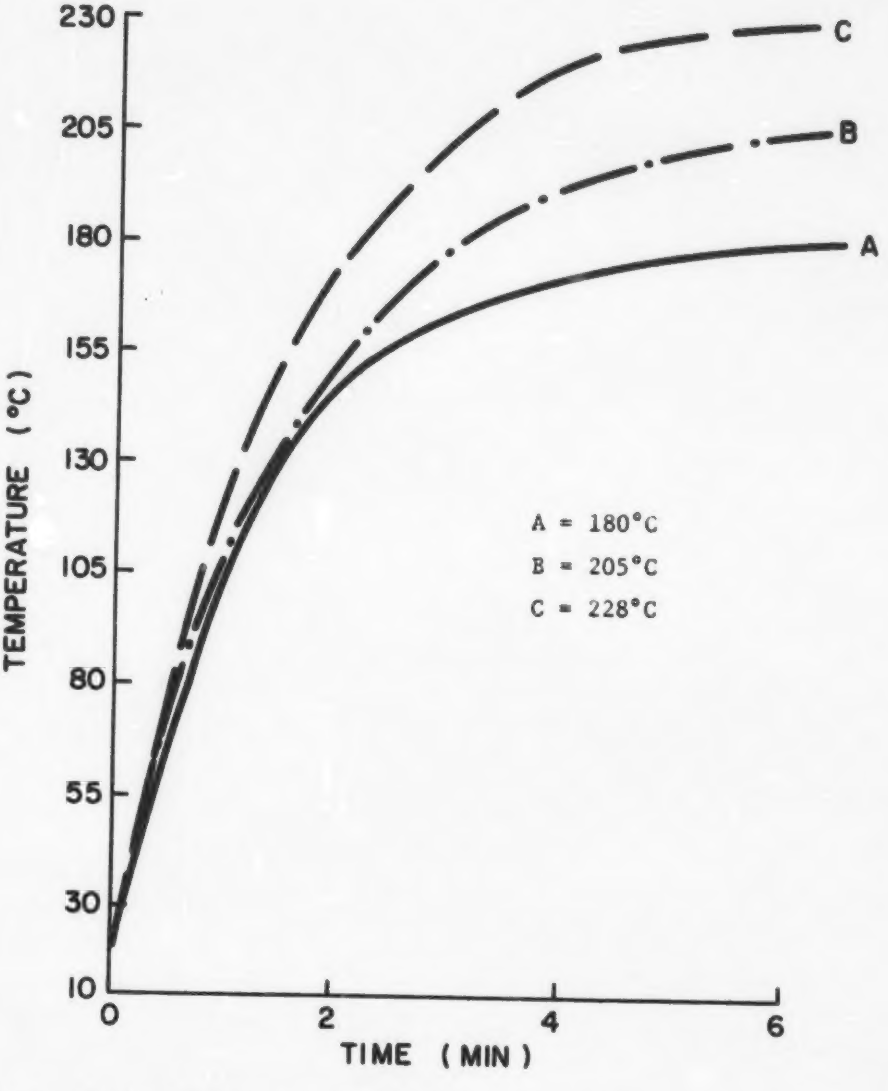


Figure 33. Heating rate for Tenax GC at different isothermal desorption chamber temperatures.

bed then the desorbed vapors may be introduced directly onto a conventionally packed glc column. The carrier gas flow rate was satisfactory for efficiently purging the desorption chamber and maintaining column resolution. Thus, the desorption chamber can be "in-line" with the glc column for a time sufficient to desorb substituents with the greatest adsorption affinities and then returned to the "by-pass" mode during the remainder of the chromatographic period. Under these conditions the background introduced during heating of the sorbent can be minimized as well as artifactual processes resulting from decomposition, polymerization, etc. of solute vapors. The use of cartridges of $\leq$ 1.0 cm i.d. and the prototype desorption chamber shown in Figure 27 allowed the inlet-manifold to be operated in the manner described.

With larger diameters, the temperature gradient in the sorbent bed was too great. In this case, a cartridge "in-line" with the glc column during the desorption cycle produced excessive solute band spreading and sample resolution was decreased. It was concluded that desorption was not uniform across the sorbent bed because of the large temperature gradient which probably accounted for the loss in glc resolution.

When sampler cartridges of > 1.0 cm i.d. were subjected to thermal desorption or high resolution capillary columns were employed, the vapors were concentrated in a small carrier gas volume in order to prevent the excessive band spreading and decreased column efficiency. This was achieved as previously described by retrapping desorped vapors in a Ni capillary (0.020 in i.d. x 0.5 m length) using liquid N_2 as the coolant. After the desorption period, the carrier gas was routed through the capillary trap (Fig. 25) and the trap rapidly heated.

SECTION VII

THERMAL DESORPTION OF HAZARDOUS VAPORS FROM SOLID SORBENTS

The recovery of vapors adsorbed or absorbed on various sorbents by thermal[16-21,28] and vacuum[45-7] desorption has been reported. Duel[46] employed a combination of vacuum-thermal stripping to remove pollutants adsorbed to cocoanut charcoal. The sample was heated from ambient to 170°C at 10°/min; partial fractionation was accomplished prior to glc analysis. Damico[32] also used cocoanut charcoal to trap glc fractions for ms analysis. Desorption of propionaldehyde and 2-nonanone occurred at room temperature and 70°C, respectively, when loaded capillaries were introduced into a high vacuum of the mass spectrometer. Other investigators also reported the thermal desorption of vapors from charcoal;[13,18,44,45] however, analysis of pollutants had been restricted primarily to aliphatic and relatively nonpolar aromatic compounds.

The high surface activity of activated carbons has been reported to produce artifacts during recovery. Formaldehyde decomposes, as does methyl ethyl ketone which forms diacetyl compounds and acetic acid. Furthermore, compounds sensitive to polymerization or decomposition on carbon are also generally sensitive to carbosieve[20,21].

Desorption of semi-polar and polar compounds by thermal means has been successively achieved from polymeric beads[15,17,20,21,38,40]. Williams[17] used temperature programming up to 210°C to elute trace contaminants from Porapak columns. Leggett, et al.[38] reported significant amounts of contaminants from Porapak was produced if the temperature exceeded 110°C during analysis. Similar results were obtained by Krumperman[16] when Porapak Q cartridges were heated above 170°C.

In contrast, Zlatkis, et al.[20,21] were able to desorb many volatile polar urine metabolites as well as atmospheric pollutants from Tenax GC at 300°C. The background from this polymer was extremely low.

Thermal desorption of trace vapors absorbed on liquid phase coated beads was extensively employed by Williams[31] for analyzing atmospheric pollutants.

Although there are many reports on the use of thermal desorption as a means for recovering and introducing the vapors into a glc, a thorough study has not been made on the quantitative aspects of this method for semi-polar and polar chemical classes of compounds such as carcinogens.

This section discusses (1) the background contribution from sorbents, (2) the desorption parameters (temperature, time) for effecting recovery for sorbents, (3) the quantification of the thermal desorption step, and (4) the percent recovery of hazardous substances of interest to this research program from Tenax GC.

EXPERIMENTAL

Tenax-GC (60/80 mesh), Chromosorb 101 (100/120), Chromosorb 104 (100/120) and Chromosorb W-HP (100/120) were purchased from Applied Science, State College, Pa. Stationary phases chemically bonded to supports which included carbowax 400/Poracil C (100/120) and oxopropionitrile/Poracil C (80/100) were also obtained from Applied Science. Carbowax 600 and didecyl phthalate stationary phases and the sorbent Porapak Q were from Supelco, Inc., Bellefonte, Pa.

Carbon derived from coke (PCB, 12/30) was acquired from Pittsburgh Activated Carbon Division of Calgon Corp., Pittsburgh, Pa. A cocoanut activated carbon (580-26) was purchased from Barneby Cheney, Columbus, Ohio.

All sorbents were thermally conditioned 10°C below the maximum recommended temperature limit for at least 12 hr under approximately 20 ml/min of He flow. After sorbents were packed into glass cartridges they were conditioned again for 15 min in the thermal desorption unit prior to use.

The standards-ethyl methanesulfonate, β-propiolactone, N-nitrosodiethylamine, 1,2-dichloroethyl ethyl ether, nitromethane, methyl ethyl ketone, and aniline - were from Fisher Chemicals, Pittsburgh, Pa. The source of glycidaldehyde and sulfolane was Aldrich Chemicals, Milwaukee, Wisc. The supply of 1,3 propanesultone, maleic anhydride, butadiene diepoxide and propylene oxide was from Eastman Organic Chemicals, Rochester, N. Y. Styrene epoxide, bis-(chloromethyl)ether and bis-(2-chloroethyl)ether were acquired from K&K labs., Plainview, N. Y.

In order to demonstrate the efficiency of collection plus thermal desorption of trapped vapors, synthetic air/vapor mixtures were prepared using N-nitrosodiethylamine (100 ng) as an internal standard; the quantity of the other vapors tested was varied from 50 to 300 ng. An aliquot of this mixture was introduced directly through the thermal desorption chamber which contained a glass cartridge packed with only glass wool and the mixture resolved by glc. The peak areas for each solute in this calibration mixture (cm) was measured by triangulation and the relative response ratios were calculated:

$$RR_{cm} = A_p/A_{is} \times \text{ng is} \qquad (5)$$

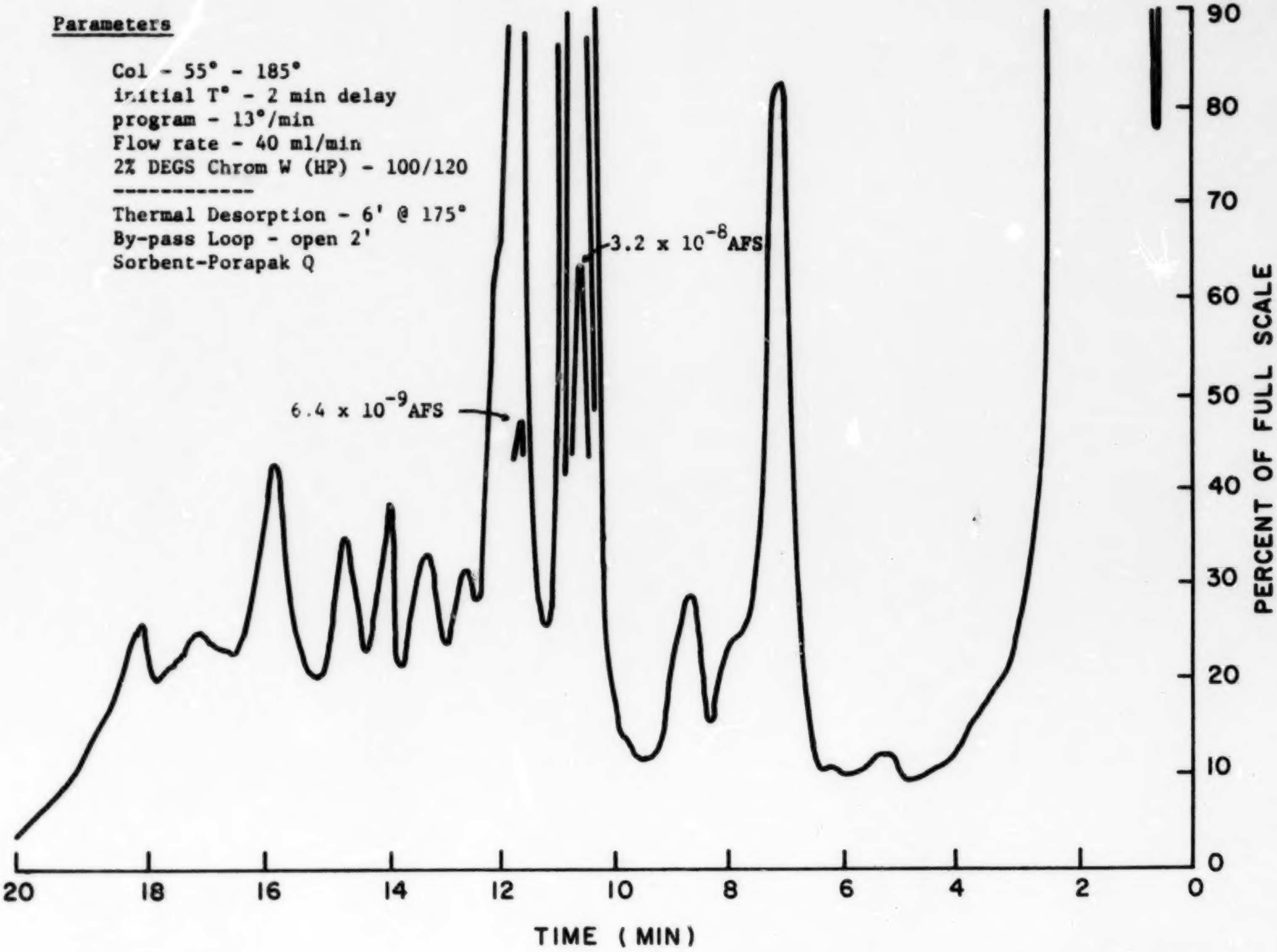
where A_p and A_{is} were the areas of the solute peak and of N-nitrosamine, respectively. An identical aliquot of the synthetic air/vapor mixture was purged (4.0 l/min) through a cartridge containing a sorbent using the monitoring system described earlier (Figure 25). The trapped vapors were desorbed in the thermal desorption chamber followed by glc analysis. The RR_s for each constituent was calculated and the percent recovery was determined as a ratio of the RR_s values to those for RR_{cm}.

$$RR_{sorbent}/RR_{cm} \times 100\% = \text{Percent recovery} \qquad (6)$$

Gas-liquid chromatography (glc) was conducted on a Perkin-Elmer 900 series chromatograph (Perkin Elmer Corp., Norwich Conn.) equipped with dual flame ionization detectors. A 2.5 mm i.d. x 3.6 m silanized glass column containing 2% DEGS on Chromosorb W(HP) 80/100 mesh was used for resolving synthetic air/vapor mixtures. The column was programmed from 55 to 200°C at 10°/min with an initial and final isothermal period of 2 and 10 min, respectively. Carrier gas (N_2), hydrogen and air flow rates were 45, 30 and 250 ml/min, respectively. The injection port, manifold and detector temperatures were maintained at 250°C.

RESULTS AND DISCUSSION

Prior to evaluating the desorption step of trace organics from sorbents, the candidate sorbents were subjected to thermal desorption temperatures; the background contribution from each was examined. The polymeric beads-Porapak Q, Chromosorb 101 and 104-all exhibited significant background even when conditioned using the manufactured recommended procedures. Of these three, Porapak Q was the worst offender (Fig. 34). These results confirm those previously reported by other investigators[16,38]. Polymeric beads were extracted in a Soxhlet for 18 hr with acetone, methanol, or benzene and then thermally conditioned; all attempts to reduce the background of Porapak Q were unsuccessful. Background was reduced significantly for Chromosorb 101 when extracted with methanol but this procedure was less successful for



Parameters

Col - 55° - 185°
initial T° - 2 min delay
program - 13°/min
Flow rate - 40 ml/min
2% DEGS Chrom W (HP) - 100/120

Thermal Desorption - 6' @ 175°
By-pass Loop - open 2'
Sorbent-Porapak Q

Figure 34. Gas-liquid chromatogram of blank Porapak-Q cartridge.

Chromosorb 104. Although Porapak Q exhibited high collection efficiencies, its background precluded any studies requiring trace analysis.

On the otherhand background contamination from Tenax GC beads was very low (Fig. 35). Pre-extraction with methanol for 18 hr followed by thermal conditioning at 325°C produced cartridges which allowed nanogram quantities of hazardous vapors to be detected and quantitated.

Sampling cartridges packed with any one of the activated carbons also exhibited low background (Fig. 36).

In contrast, inert glc supports coated or chemically bonded with liquid phases gave relatively high contaminant peaks; the latter was somewhat better. Procedures for treating these candidate sorbents to yield cartridges with low background was not exhaustively investigated. Further studies in this area are warranted, especially with phases chemically bonded to supports.

Because the desorption experiments indicated that the background contribution from Tenax GC was least of the sorbents tested, and it exhibited excellent collection efficiencies for selected hazardous substances (Section V), the thermal recovery of vapors adsorbed to this polymer was examined. Ten compounds which represent a broad spectrum of chemical properties and are of particular interest in air pollution studies were chosen. Each substance was introduced through a cartridge of Tenax GC (1.0 cm i.d. x 3.0 cm in length) at levels of 50, 100, 200, and 300 ng as a synthetic air/vapor mixture.

Initial experiments were designed to determine optimal recovery of solutes using temperatures. The principle reason was to use sufficient temperature for vaporizing the trapped constituents while minimizing sorbent background and decomposition of labile compounds or inter-compound

GLC Parameters

FID-GLC
Col. - 12 ft 2% DEGS Chrom W-HP
Program - initial hold 2 min, 70-180° @ 10°/min
Detector - 200°
Attenuation - 6.4 x 10^{-10} AFS

Thermal Desorption Parameters

Chamber - 175°
6-port Valve - 70°
Cartridge Preheat Period - 5 min
By-pass Open - 2 min

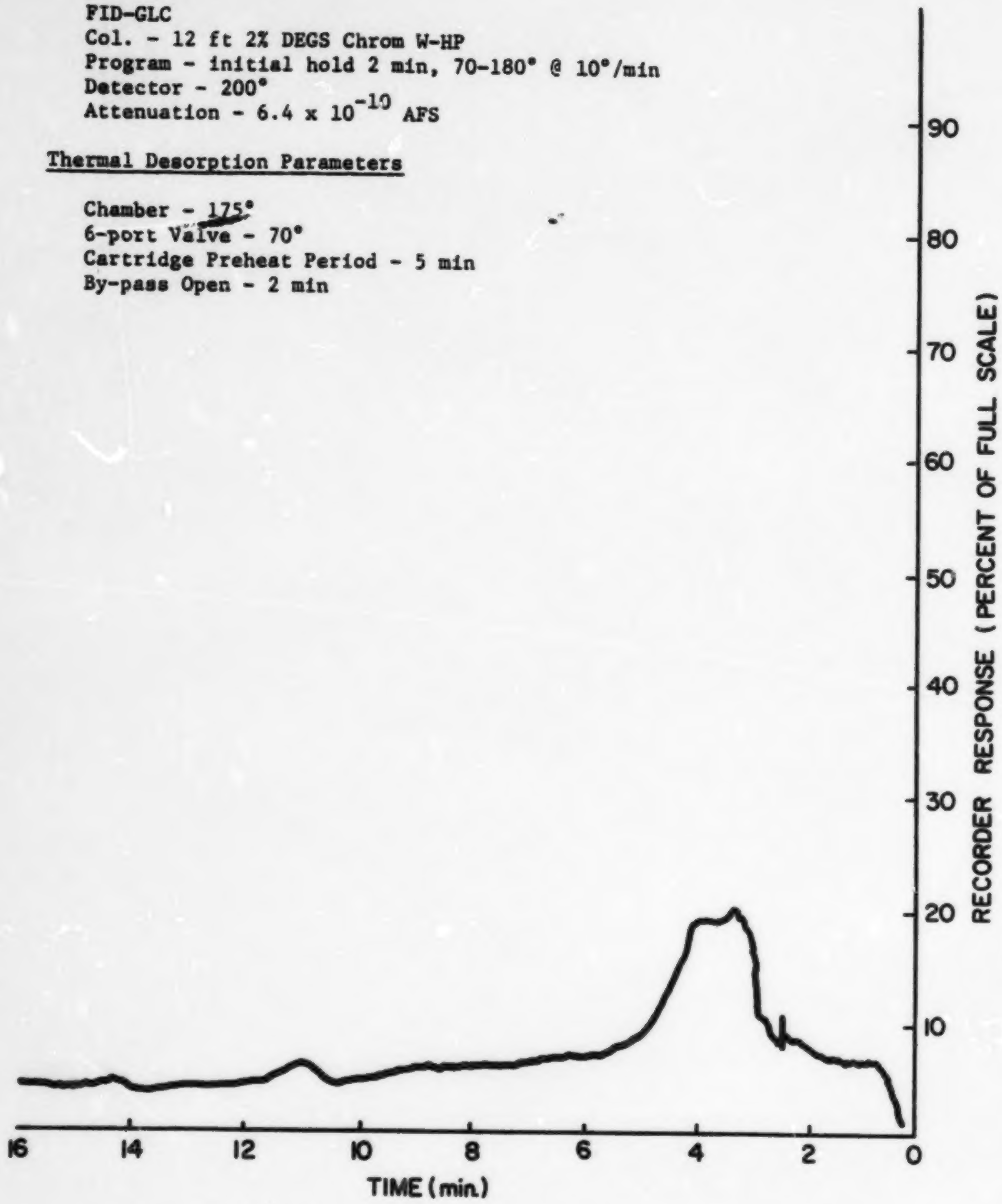


Figure 35. Background during thermal desorption of Tenax GC Cartridge Blank

GLC Parameters

FID-GLC
Col - 12 ft 2% DEGS Chrom W-HP
Program - initial hold 2 min, 70-180° @ 10°/min
Detector - 200°
Attenuation - 6.4 x 10^{-10} AFS

Thermal Desorption Parameters

Chamber - 175°
6-port Valve - 70°
Cartridge Preheat - 5 min
By-pass Open - 2 min

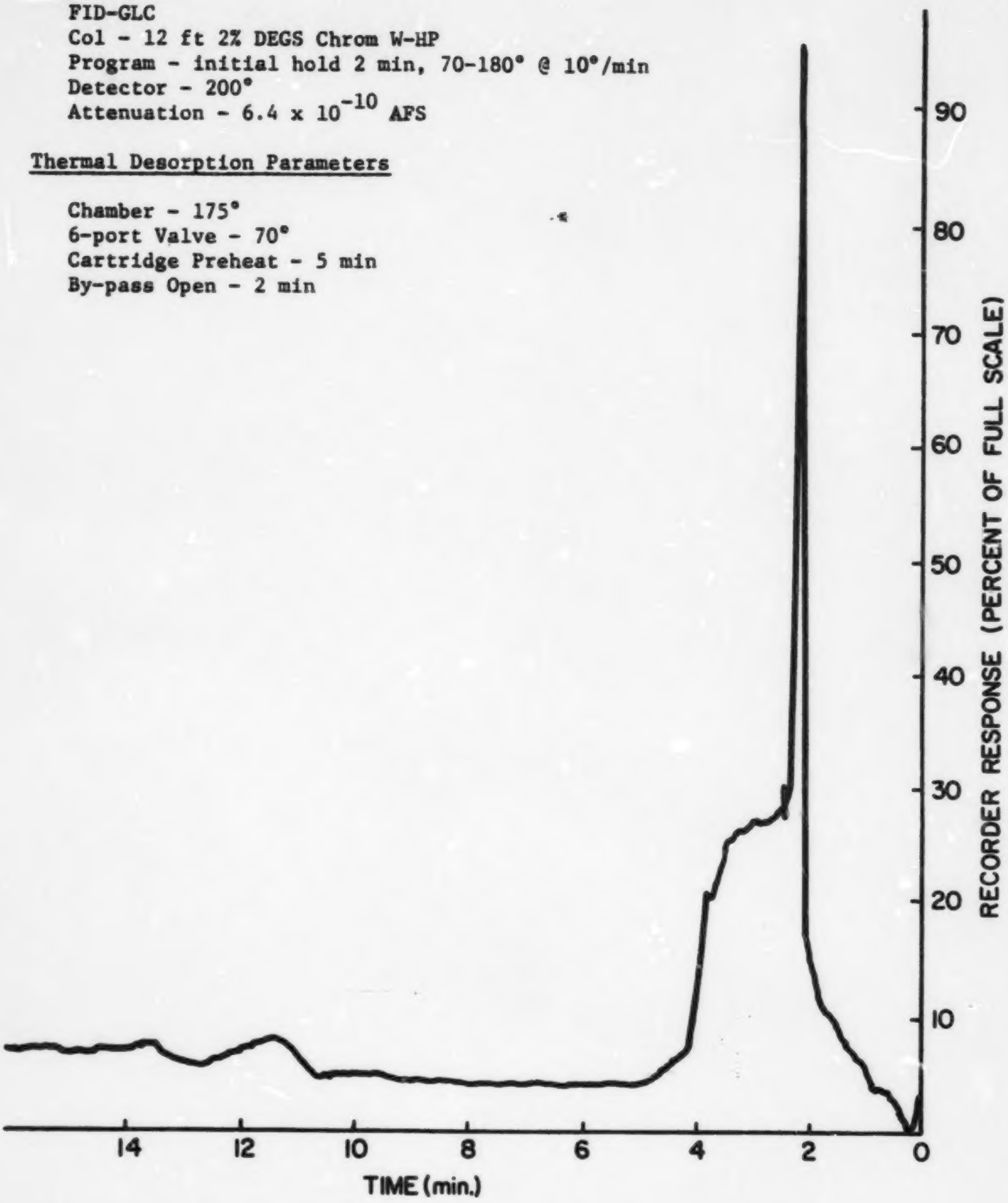


Figure 36. Background during thermal desorption of PCB carbon cartridge blank.

reactions. At a temperature of 125° relatively little amounts of vapors were desorbed from Tenax GC; 30-40% recovery was obtained at 175°C. When the desorption chamber was raised to 200°C, approximately 80-90% recovery was observed for Mixtures I, II and III (Section V).

Quantitative thermal desorption was achieved at 225°C in 90 sec. A comparison of the glc analysis for an aliquot of the synthetic air/vapor mixture used for loading a cartridge and vapors desorbed from Tenax GC is shown in Figures 37 and 38. It was concluded that none of the vapors studied had decomposed during the thermal desorption step since the chromatograms were essentially identical to those obtained for mixtures directly injected into the glc.

The percent recoveries are given in Table 18. Except for nitromethane, all of the substances examined were quantitatively recovered. Accuracy for duplicate analysis was ± 2%.

In contrast to the results obtained for Tenax GC, attempts to desorb these vapors from the activated carbons was not achieved even when temperatures up to 330°C were used; higher temperatures began to exhibit chromatographic peaks with retention indices different from the parent compounds suggesting that decomposition was occurring.

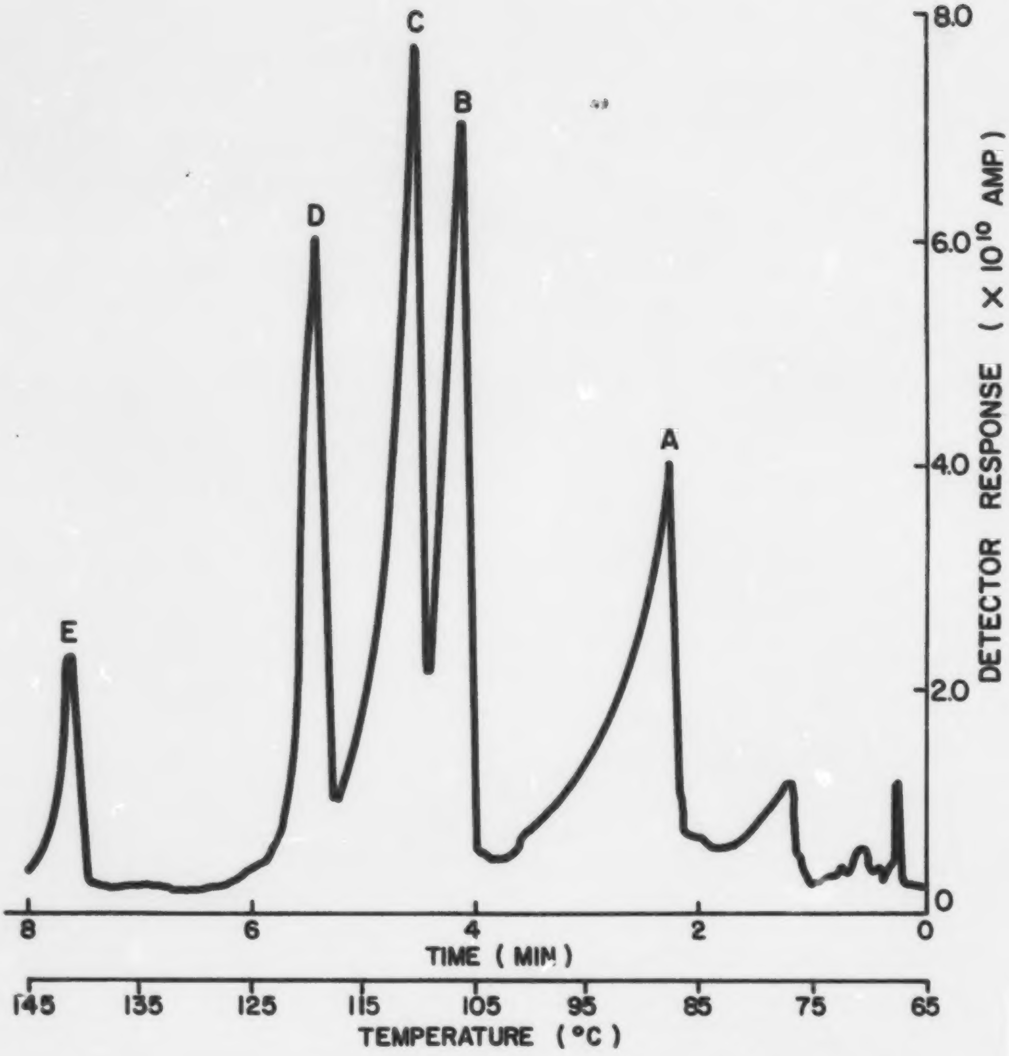


Figure 37. Gas-liquid chromatogram of synthetic air/vapor mixture of hazardous substances. Peaks A, B, C, D, and E are 300 ng of glycidaldehyde, butadiene diepoxide, N-nitrosodiethylamine, 1,2-dichloroethyl ethyl ether, and ethyl methane sulfonate, respectively. See text for glc parameters.

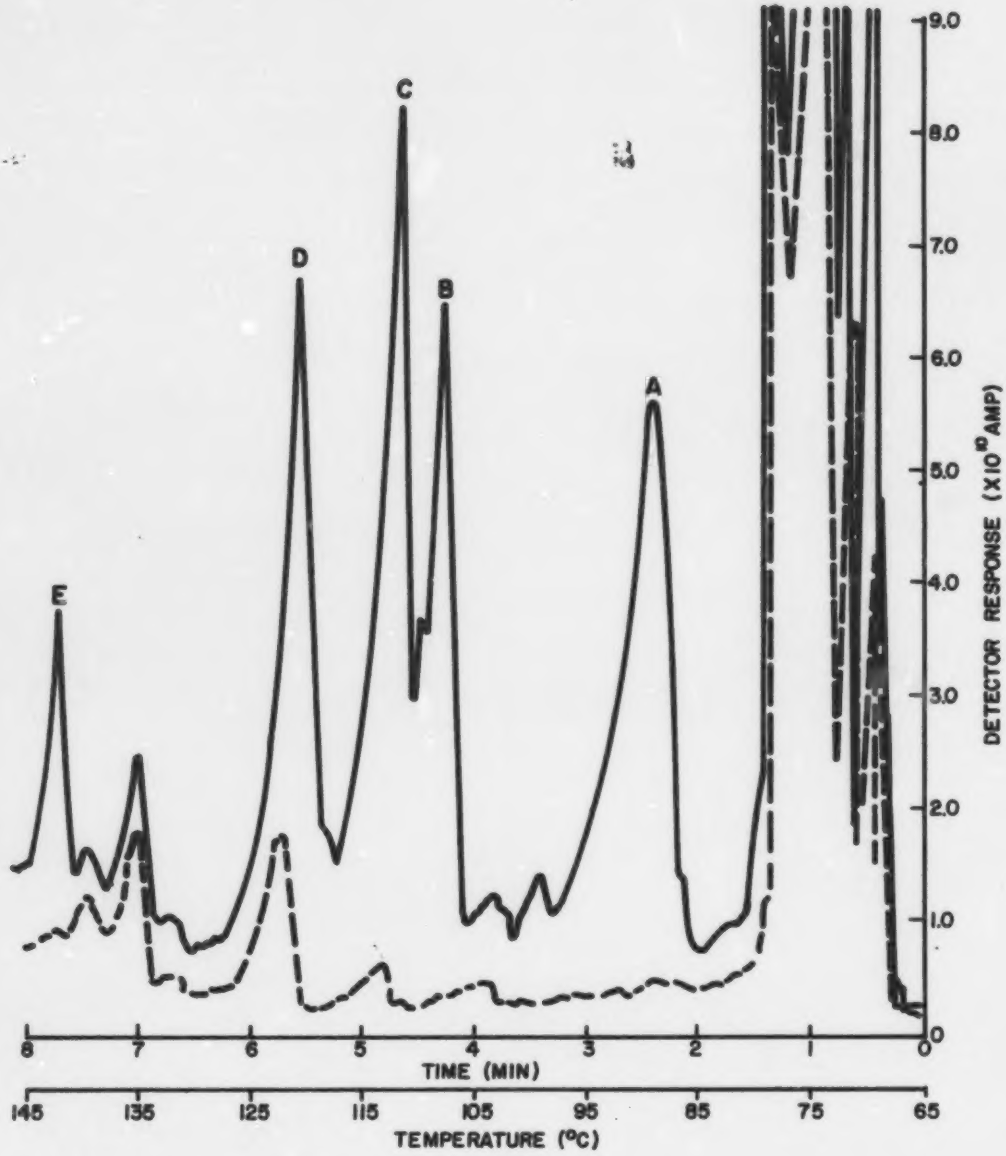


Figure 38. Gas-liquid chromatogram of vapors desorbed from Tenax GC. Desorption chamber was 225°C; see prior figure for peak identity. Background from Tenax GC is represented by dashed profile.

Table 18. PERCENT RECOVERY OF VAPORS ADSORBED ON TENAX GC CARTRIDGES USING THERMAL DESORPTION[a]

Compound	Quantity Adsorbed (ng)[b]			
	50	100	200	300
N-nitrosodiethylamine[c]	100	100	-	-
β-propiolactone	105	100	100	100
ethyl methanesulfonate	105	100	95	100
nitromethane	-	-	70	70
glycidaldehyde	100	100	95	80
butadiene diepoxide	100	100	100	100
styrene epoxide	100	100	105	90
aniline	95	95	95	60
Bis(chloromethyl)ether	100	100	100	90
Bis-(2-chloroethyl)ether	95	90	90	-

[a] Tenax GC cartridge - 10.5 mm i.d. x 30 mm in length. Synthetic air/vapor mixtures were introduced onto a Tenax GC bed @ 4 l/min. Desorption Unit was at 225°C.

[b] Represents theoretical amount in synthetic air/vapor.

[c] Values, an average of duplicate runs, were calculated on basis of a ratio of peak areas for calibration mixture and from thermal desorption.

SECTION VIII

DESIGN AND PERFORMANCE OF A FIELD SAMPLER

Collection of pollutants by other investigators has been performed at modest flow rates (20-2000 ml/min) because the concentrations of the substances sought were relatively high. In contrast, the sampling rates and time required in this research program were much greater since the hazardous vapors were anticipated at the low ng/m^3 levels. This relationship was previously shown in Table 2 (Section IV).

In order to collect sufficient quantities of each atmospheric carcinogen for instrumental analysis, the field sampling unit had to meet several requirements. These were: (1) a sampling rate adjustable from 0-3 M^3/hr at the pressure drop encountered with a sampler cartridge in-line, (2) a capability of multiple cartridges on-line during a sampling period, (3) uninterrupted 24 hr operation, and (4) the opportunity to "push" or "pull" air samples through the cartridge sampler. All of these factors ultimately determine the power (milliamps/l/min) required for sampler operation.

Also, these and additional factors were not independent of each other. Other limitations were imposed by: (1) the collection efficiencies of the packing, (2) sorbent breakthrough characteristics, (3) the lowest detectable concentrations of the carcinogenic compounds and (4) the size and shape of the cartridge sampler and how pressure differential increases with increased flow through it. Because contamination of a sample was to be avoided, the pump design was also important. Of these criteria considered in designing a field sampling unit, the pressure differential developed across a cartridge at a specified flow rate was the most important.

Questions regarding multiple sampling, continuous or pulsed flow were also considered. Flexibility, portability and durability were features sought in the unit.

The specifications for the design of a field sampling unit consisting of a pump, multiport manifold, cartridge samplers, valves and flow indicators were guided by all of the stated criteria.

This section presents a discussion of these factors individually and combined since many are interdependent.

SAMPLE VOLUME

For the purpose of developing a sampling system it was assumed that the amount of a compound required for its identification by a technique such as gas chromatography-mass spectrometry is 30-50 ng and that the sorbent was quantitative in collecting the vapors at low concentrations. The relationships between the ambient vapor concentration and the total volume of air that must be pumped through the cartridge, and thus, the time required for sampling, at various flow rates were given in Table 1. The total power required for sampling was directly related to sampling rate and duration.

POWER REQUIREMENT

The power required to pump air through sorbent-packed tubes depends upon the pressure differential across the tube under flow conditions, which in turn depends mostly upon the air flow-rate, the shape of cartridge (diameter and depth of packing), the particle size distribution, and the particle shape of the sorbent, and to a lesser extent upon the air temperature and humidity. A method for calculating power requirements from pressure drop values was developed for this study.

From the values of p_1 and p_2 in equation (4), the theoretical power (watts) required for compression or expansion of the air (compression if the sampler were downstream from the pump) and its delivery through the sampler was estimated using a formula derived from the Moss and Smith equation for adiabatic horsepower. The formula employed was:

$$\text{Power (Watts)} = \ell/m \times 5.968 \times [(p_1/p_2)^{\frac{k-1}{k}} - 1] \quad (7)$$

where ℓ/m = liters per min, p_1 and p_2 are the high and low pressures across the sampler, and k is the ratio of specific heats for air, c_p and c_v. This formula is based upon air at 14.7 psi, 23°C and 36 percent relative humidity; its density was taken at 0.075 lb/ft^3; k was set at 1.3947.

Figure 39 shows the theoretical power required to pump air through 5-cm depths of sorbent packing. For a flow-rate of 20 liters/min, the change from 60/80 mesh particles to 18/20 in the 1.06 cm tube reduces power requirements by almost a factor of 5 (30.4 watts to 6.4). Increasing the tube diameter from 1.06 cm to 1.82 cm decreases power for the 60/80 mesh packing from 30.4 to 21 watts. From these data it was concluded that tube diameters of approximately 1.5 cm, particles of about 35/60 mesh, and bed depths of about 5 cm will allow sampling rates of 20 liters/minute for a theoretical power consumption of 15 watts (0.02 horse power). Practical power requirements are expected to be at least twice the theoretical values to allow for power losses in the pump itself. For example, a cartridge of Tenax GC, 35/60 mesh, in a 1.82-cm tube would require twice the theoretical 7,4 watts, or 14.8 watts to sample air at 20 ℓ/m.

While the power requirements can be supplied by almost any 115 V, 50-60 Hz source, the power ratings of portable battery powered samplers would have to be increased substantially to permit their use at low

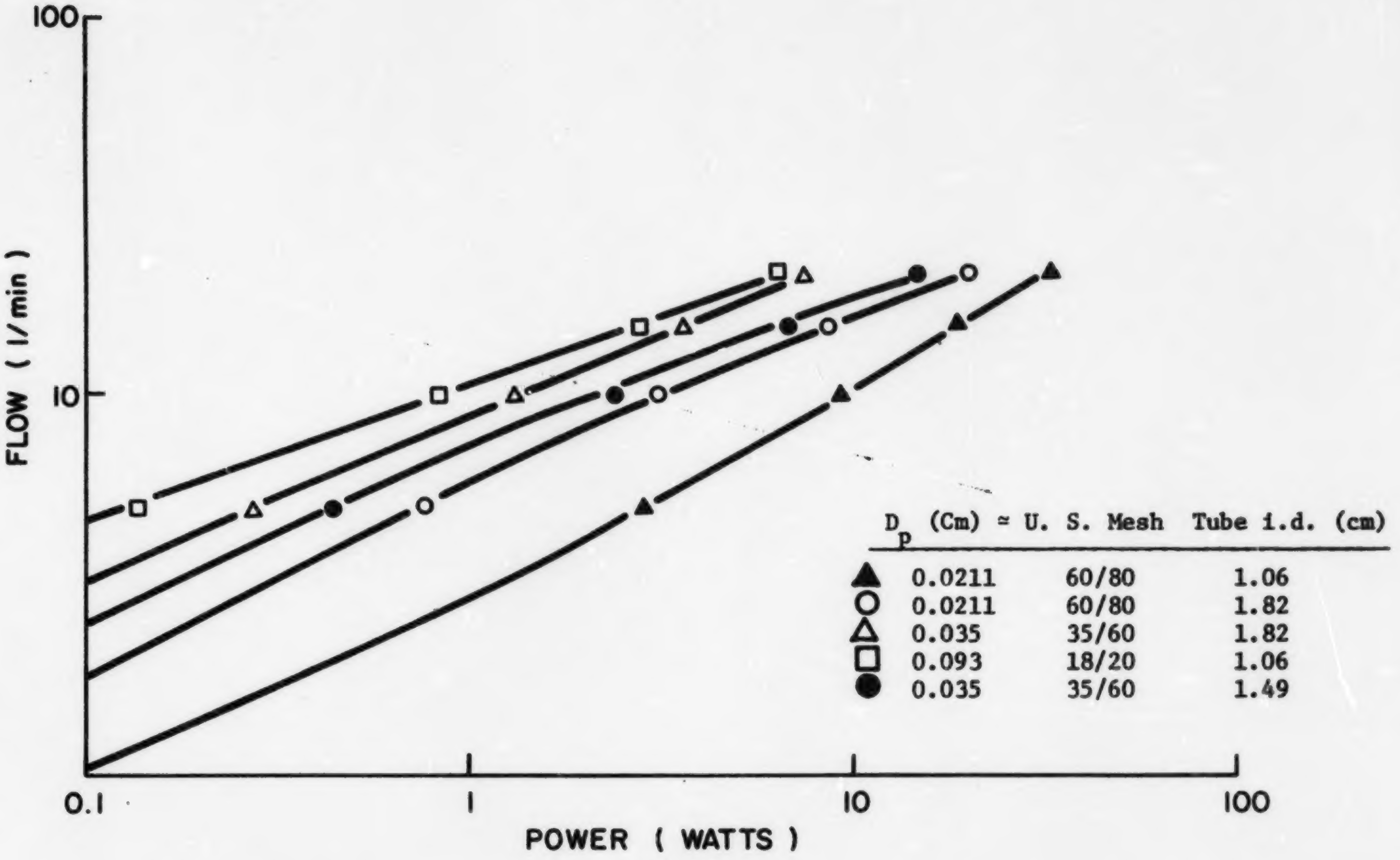


Figure 39. Relationship between flow rate and theoretical power requirements at various tube diameters and particle size.

concentrations and sampling rates. The required 6-volt battery ratings for a sampler with a 5-cm depth of Tenax GC 30/65 in a 1.8 cm tube are given in Table 19.

With the exception of nickel-cadmium batteries, which provide up to 45 mA for 10 hours, most of the sampling would therefore involve the use of several batteries, possibly, in parallel, with recharging at regular intervals, determined by the specific case. The use of battery operated samplers in detecting ng/m^3 concentrations of organic vapors depends upon the effectiveness and capacity of sorbents with particle sizes in the 12/30 mesh range. Pressure-drops at high flows (20 ℓ/m) must be kept low to avoid vacuum desorption if the air sample is drawn through the cartridge.

FLOW VECTOR REQUIREMENTS

Whether the pumping unit would best serve in the capacity of pulling or pushing the atmosphere through the cartridge also depended upon the pressure differential developed. For instance, if a large pressure drop

Table 19. POWER REQUIREMENTS TO DELIVER VARIOUS SAMPLING RATES

Sampling Rate ℓ/min	Power Needed Watts	Six-Volt Battery Capacity Required Per Sample millamp-hr			
		ng/M^3			
		1	10	100	1000
1	0.022	1800	180	18	1.8
4	0.34	7500	750	75	7.5
9	2.06	19150	1915	192	19.2
20	14.8	61500	6150	615	61.5

(> 100 mm Hg) was required to attain the desired sampling flow rates then a "pull" system may significantly decrease the collection efficiency profiles for each sorbent (vacuum stripping). Since collection efficiencies in our studies have been acquired under positive pressure ("push") then a "push" sampling system would deliver the best correlation between field and laboratory trials.

A continuous flow pumping unit was preferred to a pulse system since the latter may have disturbed the packing material in the cartridge and/or differ in trapping characteristics from those observed by our continuous flow system in laboratory experiments. A separate examination of collection efficiency and breakthrough volumes would be necessary in order to determine the merits of pulse sampling. Such a study was not conducted.

REPLICATE SAMPLING

The uncertainties inherent in sampling for the hazardous organic vapors imposed a need for a versatile system for multiple sampling, i.e., taking several simultaneous samples. For example, acquisition of duplicate samples simultaneously circumvented the problem associated with diurnal fluctuations of vapor concentrations occurring when duplicates were obtained sequentially. Furthermore, different collection media could be compared by sampling the same atmosphere concurrently. The ability to collect with several cartridges at one time was conducive to overall shorter field sampling periods as well as comparison of sample duration vs breakthrough (Section V).

To draw 25 ℓ/m of air through two sets of two samplers in parallel, each containing a 3-cm depth of 0.035-cm diameter adsorbent in a 1.06-cm diameter tube, the pump must draw 50 ℓ/m at a pressure drop of 8.34 N/cm^2 (626 mm Hg). On the other hand it was also desirable to use cartridges in tandem to determine whether breakthrough has occurred. The Universal

Sampler 5 1068 (Research Appliance Co., Allison, Pa.) met these requirements and has been used in our field sampling studies. Its operation required approximately 1/2 h.p. at 110 V, 50-60 Hz. This unit is shown in concept in Figure 40.

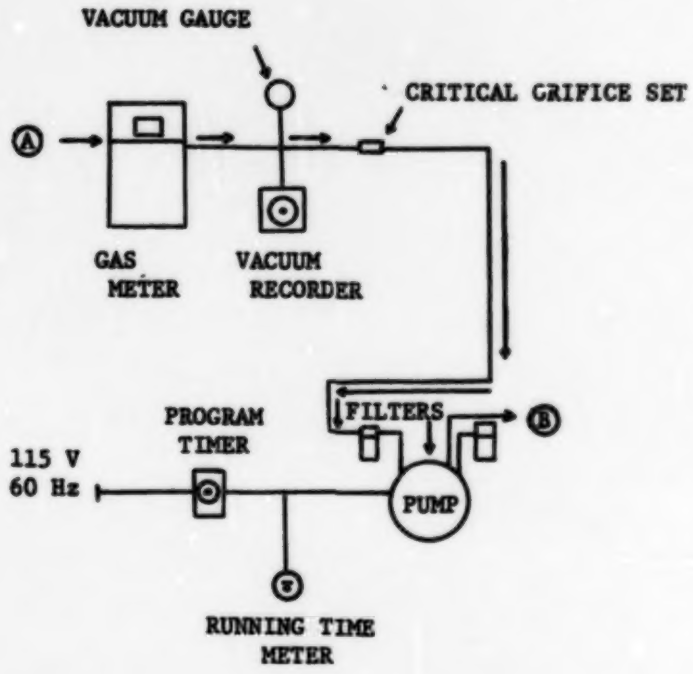

VACUUM GAUGE
CRITICAL ORIFICE SET
Ⓐ
GAS METER
VACUUM RECORDER
PROGRAM TIMER
FILTERS
Ⓑ
115 V
60 Hz
PUMP
RUNNING TIME METER

Figure 40. Schematic of Universal Sampler 5-1068

The "pull" sampler would go at "A"; the push sampler, if employed, at "B". This system consists of those elements that will provide control of the sampling at desired rates. The system was quantified for a range of flow rates up to 25 liters per minute, using the sampler employed in testing adsorbents (a 3 cm deep packing of 0.035 cm diameter adsorbent in a 1.06 cm diameter tube). Calculations showed that, to draw (or push) 25 l/m of air through two sets of two samplers in series, the pump must draw 50 l/m (1.76 cfm) at a pressure drop of 8.34 N/cm^2 (12.1 psi).

In order to accommodate the use of multiple cartridges during a sampling period, a multiport chamber was designed and fabricated (Fig. 41). The entire chamber was constructed of Teflon®. Six ports were located on the chamber equidistant from one another (60°) so that any multiple of 1,2,4, and 6 sampling cartridges could be employed simultaneously without experiencing different drawing rates since a symmetrical geometry was maintained. The air was drawn through a glass fiber filter (to remove "particulates") and the cartridge, into the multiport head and then through the pumping system. The sampling rate through the cartridges was regulated by a bleed valve located on the multiport chamber. A vacuum/pressure gauge on the chamber was used to monitor the pressure differential and by consulting the pressure drop curves, a ΔP was selected and imposed in the chamber which produced the desired sampling rate through each cartridge.

The multiport chamber was utilized with the Universal sampling pump. Table 20 depicts the maximum sampling rates which this system is capable of achieving under various conditions (bleed valve closed). When four cartridges of Tenax GC (60/80) are compared to the same number of Chromosorb 101 (100/120), the vacuum required to draw equivalent rates per cartridge (and therefore total flow) was increased by 75 mm Hg. This observation corroborates the experimentally determined ΔP for various particle diameters. The magnitude of the vacuum required to achieve a prescribed sampling rate may ultimately influence the performance of the sorbent. Decreased collection efficiencies and/or elution volumes may be experienced.

The design parameters and systems described in this and previous sections were applied to the collection of trace quantities of hazardous pollutants in ambient atmospheres.

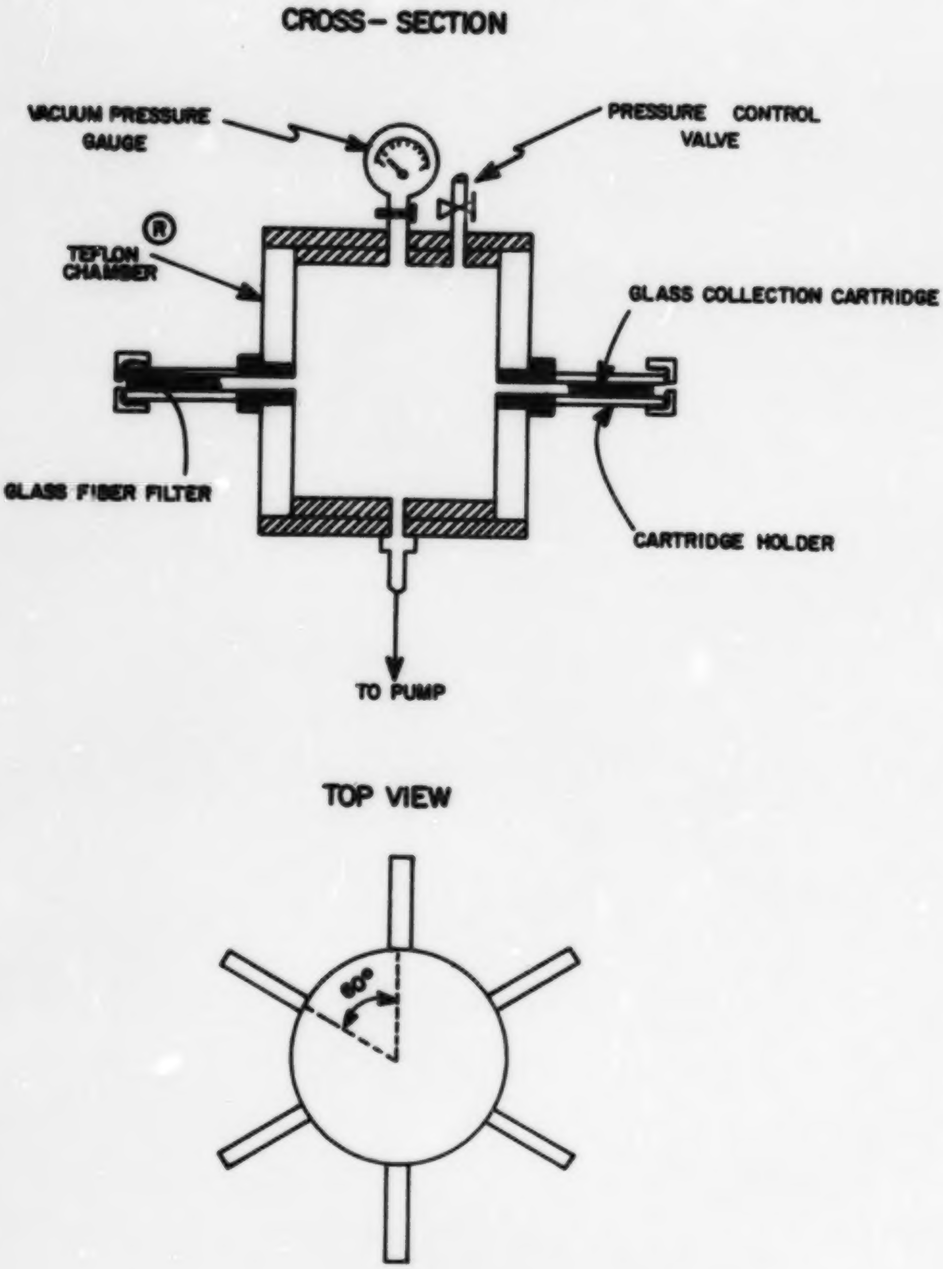

CROSS- SECTION
VACUUM PRESSURE GAUGE
PRESSURE CONTROL VALVE
TEFLON® CHAMBER
GLASS COLLECTION CARTRIDGE
GLASS FIBER FILTER
CARTRIDGE HOLDER
TO PUMP
TOP VIEW
60°

Figure 41. Multiport sampling head.

Table 20. SAMPLING RATE CHARACTERISTICS FOR UNIVERSAL SAMPLER[a] WITH MULTIPORT HEAD

Sorbent	No. of Cartridges[b]	Sampling Rate		Total Volume m^3/hr
		1/min/cartridge	m^3/hr/cartridge	
Tenax GC (35/60)	1	77.0	4.62	4.62
	2	41.5	2.49	4.98
	4	21.5	1.29	5.15
	6	14.7	0.88	5.28
Tenax GC (60/80)	1	76.5	4.59	4.59
	2	41.2	2.47	4.94
	4	21.6	1.29	5.18
	6	14.6	0.88	5.27
Chromosorb 101 (100/120)	1	74.7	4.49	4.49
	2	40.5	2.29	4.48
	4	21.4	1.28	5.13
	6	14.5	0.87	5.23

[a] The maximum pumping rate (no flow restriction) for this commercial system is 89 1/min (5.28 m^3/hr).

[b] Cartridge dimensions were 1.56 cm i.d. x 6.0 cm in length.

SECTION IX

APPLICATION OF DEVELOPED INSTRUMENTATION AND METHODOLOGY TO THE ANALYSIS OF AMBIENT AIR

In previous sections of this report detailed experimental design and techniques were described for collecting and analysis of hazardous vapors. Preliminary results on the application of this methodology and instrumentation to field sampling and the analysis of air samples by combined gas-liquid chromatography/mass spectrometry/computer are discussed in this section.

EXPERIMENTAL

Site of sampling

An urban site which presumably was concentrated with automobile exhaust in the presence of strong sunlight was chosen. An environment conducive to photochemical smog is known to exhibit high levels of ozone, NO_2 and NO_x. Two sites which had a history of high levels of ozone were at the CHAMP stations in Santa Monica and West Covina, CA[57]. Furthermore, West Covina during the month of April, 1974 also had appreciable amounts of NO_2 and NO_x. On the basis of the presence of these pollutants and aliphatic and aromatic hydrocarbons in air, the possibility of the formation of epoxides and nitrosamines forming in ambient air was suspected to occur.

Sample Collection

Ambient air samples were collected with a Universal Sampler 5-1068 equipped with a multiport head as described in Section VIII. The sorbents selected for the collection of pollutants were Tenax GC and Chromosorb 101 which was based upon their performance described in Section V. The samplers (cartridge holders plus glass cartridges) were prepared in the laboratory, transported by air freight to Los Angeles, CA, and after sampling was completed, returned also by air freight.

The protocol used for collecting air pollutants for glc-ms-comp analysis is shown in Table 21 (additional experiments performed at these sites were described in Section V under breakthrough). Replicate samples were acquired which represented 2-6 m^3 of processed air. Because it was uncertain at what concentration levels the background pollutants would occur, analyses included low and high volumes of air; in some cases the desorbed vapors of several cartridges were combined prior to glc-ms-comp analysis.

The vapors of two internal standards, methyl ethyl ketone and nitrobenzene, were introduced into some of the cartridge samplers at the beginning of a sampling period. These standards were used for obtaining relative retention data for the pollutant peaks detected during glc-ms, as well as ascertaining the relative breakthrough and transportation effects.

Gas liquid chromatography/mass spectrometry/computer

The instrumental systems used in this study are shown in Figure 42. The inlet-manifold used for recoverying vapors trapped on sorbents was the same as shown in Figure 25. The desorbed vapors were subsequently resolved by gas-liquid chromatography and mass cracking patterns were automatically and continuously obtained throughout the glc run with a Varian CH-7 mass spectrometer. The cracking patterns and retention time data were accumulated on a magnetic tape deck and further processed by an "on-line" Varian 620i computer. Computer programs (KOSL) were employed which converted the acquired spectra into a sequential series of mass spectra and were correlated to peak retention time on a total ion current plot (Fig. 43). Data output from the 620i computer were provided in two forms: (1) a teletype listing which contained the mass spectrum number, the number of peaks in the cracking

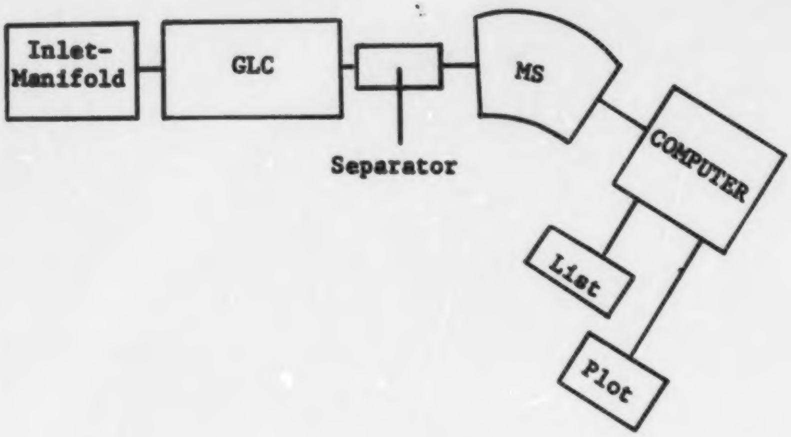

Inlet-
Manifold
GLC
Separator
MS
COMPUTER
List
Plot

Figure 42. Gas-liquid chromatograph-mass spectrometer computer (GLC-MS-COM) outlay.

pattern total maximum and minimum m/e peak intensity, and standard deviation from calibrated m/e, and (2) an electrostatic plot of total ion current plots and/or normalized mass spectra.

The operating parameters for the glc-ms-comp system for the analysis of cartridges containing trapped pollutants are given in Table 22. These conditions were used throughout this entire study.

RESULTS AND DISCUSSION

Figure 43 represents a total ion current plot from the mass spectrometer for an air sample from West Covina, CA. This profile was typical for samples also collected in Santa Monica. The identity of several peaks are given in Table 23 for this sample and Table 24 for a Santa Monica sample. The major constituents were aromatics and aliphatics. One oxygenated compound, tenatatively identified as styrene epoxide in this sample, was not detected in samples from Santa Monica. Styrene, itself, was likewise not detected; however, methylvinyl benzene was present. Styrene was reported in Houston air by Bertsch et al.[20]; styrene epoxide was not. The discovery of styrene epoxide was the most significant finding in this entire study.

Mass spectra were also obtain of the background from Tenax GC (35/60); it was concluded that ethylene oxide was an artifact generated from thermal desorption of this sorbent.

Because it was evident that the majority of the constituents were aliphatics and aromatics, single ion plots of 71 and 85 (Fig. 44) and 91, 105, 120, and 134 (Fig. 45) were obtained to demonstrate their distribution pattern throughout a chromatogram. The low intensities of the aliphatic ions (Fig. 44) indicated that some selectivity was exhibited by the Tenax GC cartridge, i.e. it was less effective in trapping aliphatic compounds than aromatics or polar pollutants. This selectivity was desirable because the

Table 21. PROTOCOL FOR SAMPLING AMBIENT AIR IN LOS ANGELES, CA

Experiment	Cartridge Type	Sampling parameters			Location	Remarks
		time (hr)	rate (l/min)	volume (m^3)		
1	Tenax GC (35/60) 1.5 cm i.d. x 6 cm				Santa Monica, CA	——
	A	5	24	6.6		
	B	5	24	6.6		
2	Tenax GC (35/60) 1.0 cm i.d. x 3 cm					
	A	3	12	2.07	West Covina	+ internal standards-- MEK & NB
	B	3	12	2.07		
	C	3	12	2.07		
	D	3	12	2.07		
3	Chromosorb 101 (60/80)					
	A	3	12	2.07	West Covina	+ internal standards- MEK & NB
	B	3	12	2.07		
	C	3	12	2.07		
	D	3	12	2.07		

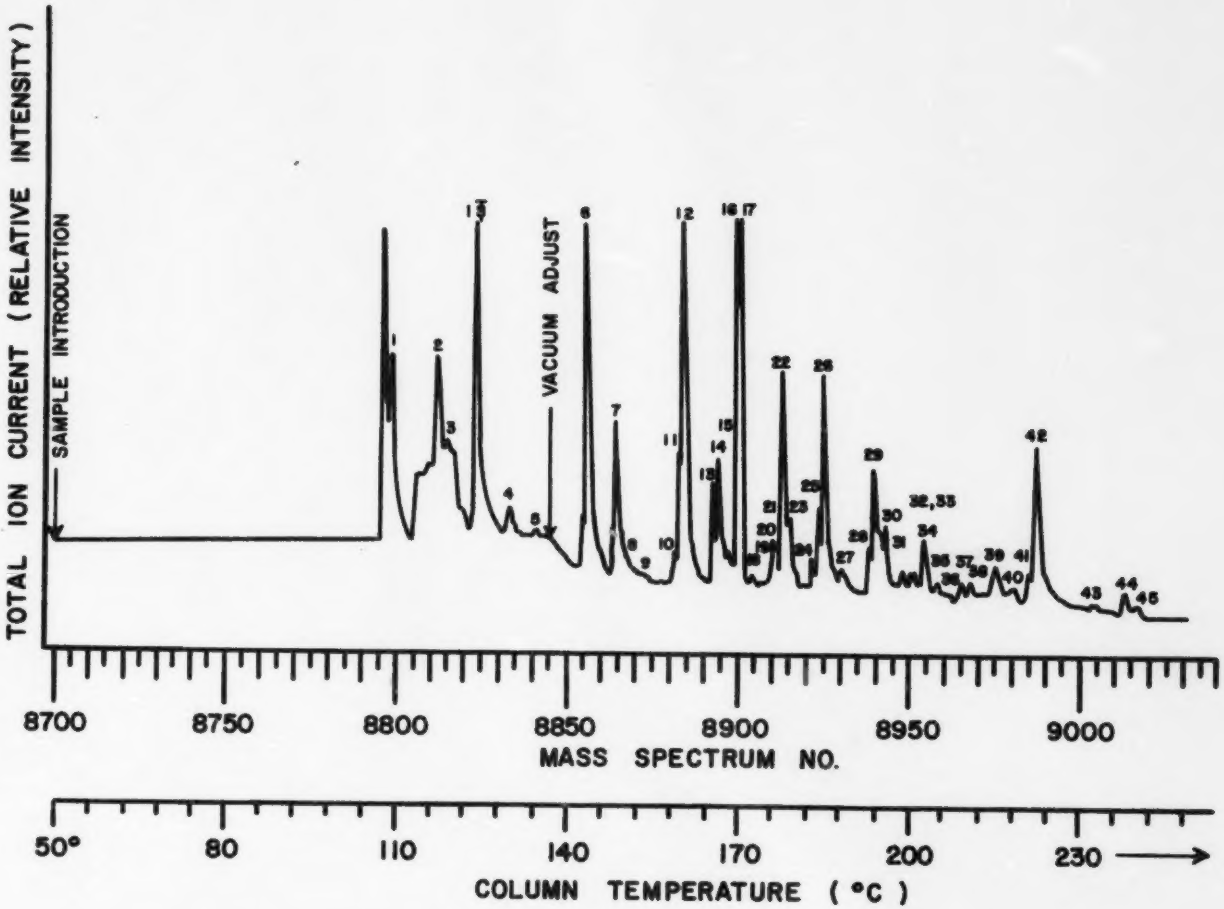


Figure 43. Total ion current plot during gas-liquid chromatography mass spectrometry of air sample from West Covina, CA. See text for conditions.

Table 22. OPERATING PARAMETERS FOR GLC-MS-COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber	225°C
valve	125°C
Capillary trap - minimum	-195°C
maximum	+175°C
thermal desorption time	4 min
GLC	
OV-17 Ni capillary, 450 ft	
column	50-230°C, 4°C/min
carrier (He) flow	~3 ml/min
transfer line to ms	210°C
MS	
scan range	m/e 20 → 300
scan rate, automatic-cyclic	1 sec/decade
filament current	300 μA
multiplier	6.0
ion source vacuum	~4 x 10^{-6} torr

Table 23. POLLUTANTS IN AMBIENT AIR FROM WEST COVINA, CA

Peak No.	RRT	Name
1	0.793	ethylene oxide
2	0.900	acetone
3	0.930	methylene chloride
4	1.077	2,4-dimethylpentane
5	1.087	nor-heptane
6	1.261	toluene
7	1.320	unknown
8	1.330	tetrachloroethylene
9	1.350	C_{10} branched alkanes
10	1.465	C_{10} branched alkanes
11	1.485	nordecane (tent.)
12	1.505	p-xylene
13	1.562	m-xylene
14	1.570	o-xylene
15	1.600	unknown
16	1.630	propylbenzene
17	1.635	methyl ethyl benzene
18	1.650	unknown
19	1.670	unknown
20	1.699	styrene oxide (tent.)
21	1.715	unknown
22	1.726	methyl ethyl benzene
23	1.747	unknown
24	1.795	methyl ethyl benzene
25	1.815	2-methyldecane
26	1.825	C_3 alkyl benzene
27	1.874	unknown
28	1.930	trimethyl benzene
29	1.950	methyl ethyl benzene
30	1.970	unknown
31	2.010	methylvinylbenzene

Table 23 (continued). POLLUTANTS IN AMBIENT AIR FROM WEST COVINA, CA

Peak No.	RRT	Name
32	2.030	dimethylethylbenzene
33	2.035	dimethylethylbenzene
34	2.059	methyldiethylbenzene
35	2.070	n-tridecane (tent.)
36	2.150	unknown
37	2.162	$C_{14}H_{30}$
38	2.178	tetramethylbenzene
39	2.233	p-tolualdehyde
40	2.261	acetophenone
41	2.310	unknown
42	2.330	nitrobenzene
43	3.380	unknown
44	3.530	naphthalene
45	3.561	unknown

Table 24. POLLUTANTS IN AMBIENT AIR FROM SANTA MONICA, CA

Peak No.	RRT	Name
1	0.835	unknown
2	0.873	unknown
3	0.888	acetone
4	0.910	methylene chloride
5	0.949	dimethylpentane
6	0.963	nor-heptane
7	0.977	unknown
8	0.993	unknown
9	1.0	methyethylketone
10	1.082	dimethylpentane
11	1.153	nor-octane
12	1.166	1-octene
13	1.270	toluene
14	1.325	tetrachloroethylene
15	1.335	nor-nonane
16	1.459	ethylhexylketone (tent.)
17	1.472	p-xylene
18	1.550	unknown
19	1.559	m-xylene
20	1.570	o-xylene
21	1.610	unknown
22	1.642	unknown
23	1.666	nor-propylbenzene
24	1.677	methylethylbenzene
25	1.690	styrene oxide (tent.)
26	1.745	unknown
27	1.765	trimethylbenzene
28	1.850	unknown
29	1.870	unknown
30	1.952	unknown
31	1.979	unknown
32	2.090	unknown

Table 24 (continued). POLLUTANTS IN AMBIENT AIR FROM SANTA MONICA, CA

Peak No.	RRT	Name
33	2.161	acetophenone
34	2.330	nitrobenzene

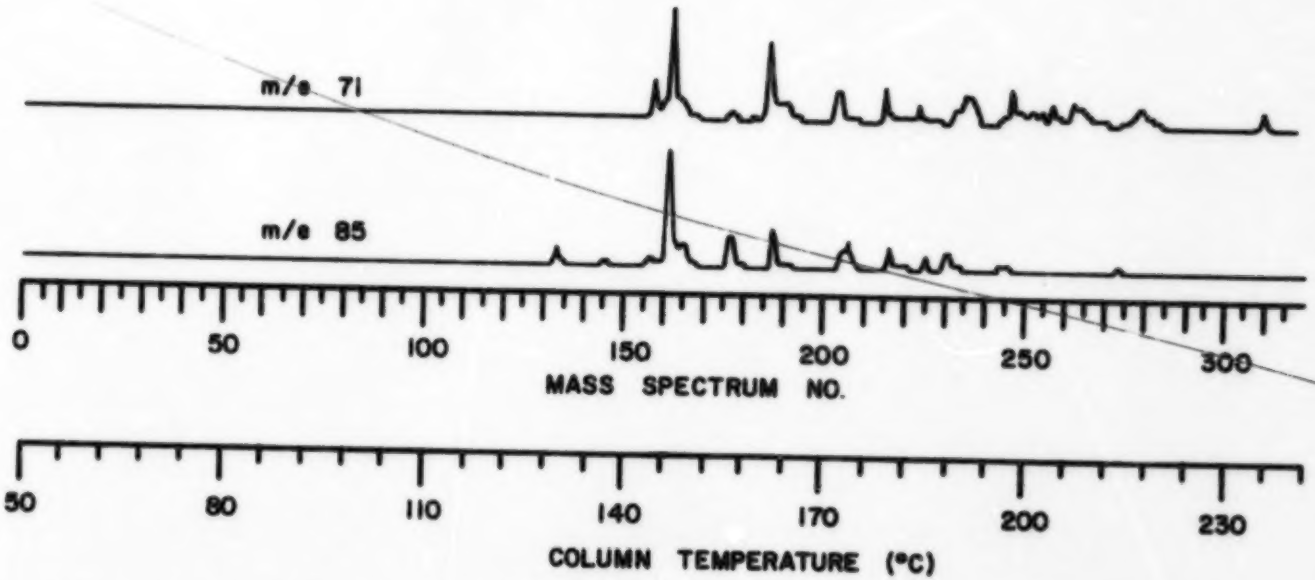


Figure 44. Single ion plots of ions common to aliphatic cracking series.

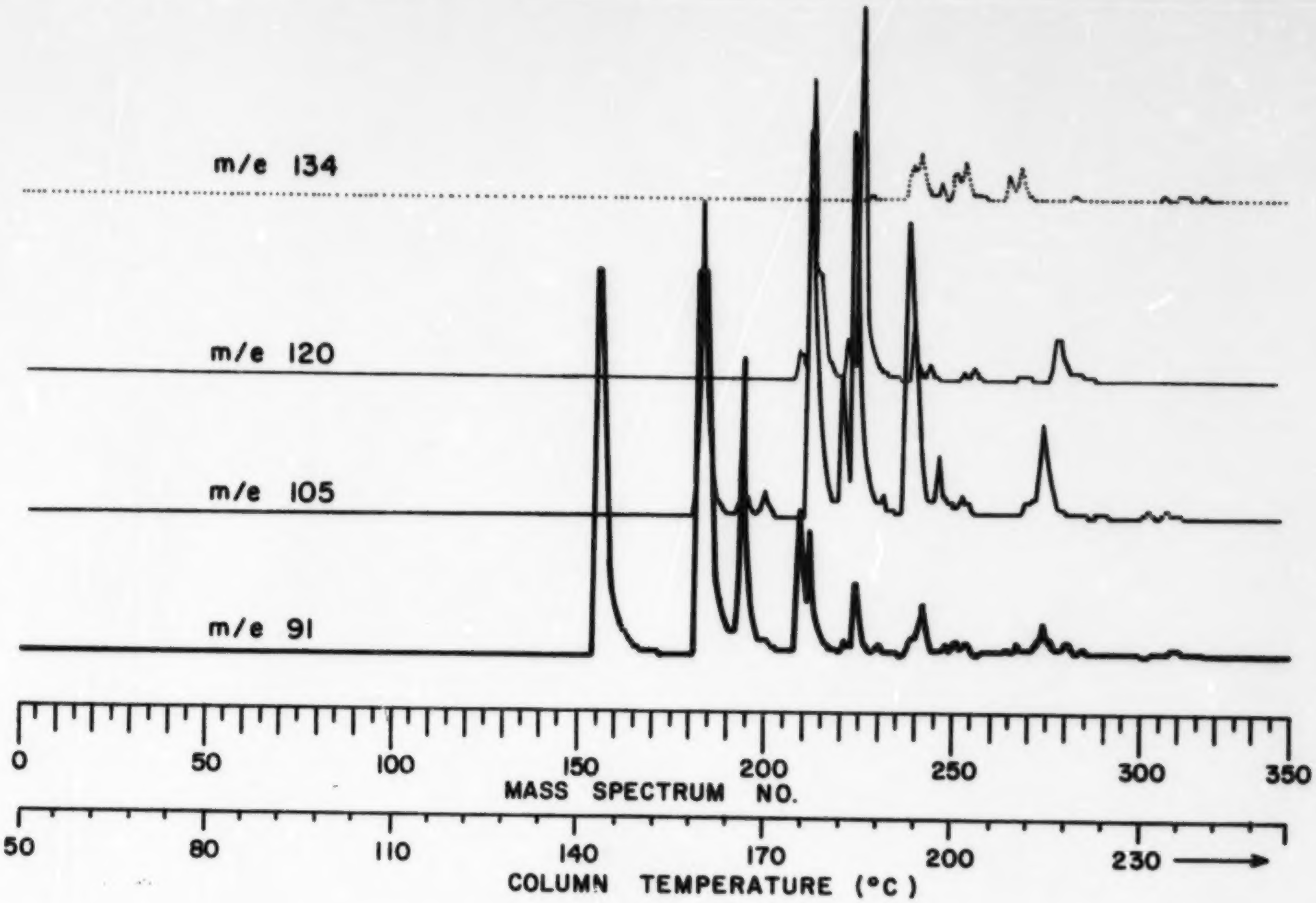


Figure 45. Single ion plots for ions representative of aromatic cracking series.

hazardous vapors which are to be collected and identified under this program are considered to be semi-polar to polar.

In contrast the intensities of aromatic ions (Fig. 45) were relatively large and constituted a high background between 140° to 230° which impeded the detection and identification of possible hazardous vapors occurring at trace levels. It was concluded that the chromatographic conditions should be improved whereby the aliphatic and aromatic compounds are resolved as a group from hazardous vapors of interest. The use of more polar stationary phases and longer high resolution columns are currently under investigation.

SECTION X

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SECTION XI

LIST OF PAPERS ACCEPTED OR SUBMITTED FOR PUBLICATION

1. COLLECTION AND ANALYSIS OF TRACE ORGANIC VAPOR POLLUTANTS IN AMBIENT ATMOSPHERES

   I. A Technique for Evaluating the Concentration of Vapors by Sorbent Media.

   E. D. Pellizzari, J. Bunch, B. Carpenter and E. Sawicki

   J. Environmental Science and Technology. Accepted for Publication.

2. COLLECTION AND ANALYSIS OF TRACE ORGANIC VAPOR POLLUTANTS IN AMBIENT ATMOSPHERES.

   II. Studies on Thermal Desorption of Organic Vapors from Sorbent Media

   E. D. Pellizzari, B. Carpenter, J. Bunch and E. Sawicki

   J. Environmental Science and Technology. Accepted for Publication.

3. COLLECTION AND ANALYSIS OF TRACE ORGANIC VAPOR POLLUTANTS IN AMBIENT ATMOSPHERES

   III. The Design of a Sampler System for Trace Quantities of Organic Vapors

   B. Carpenter, E. D. Pellizzari, J. Bunch and E. Sawicki

   J. Environmental Science and Technology. Submitted for Publication.

APPENDIX

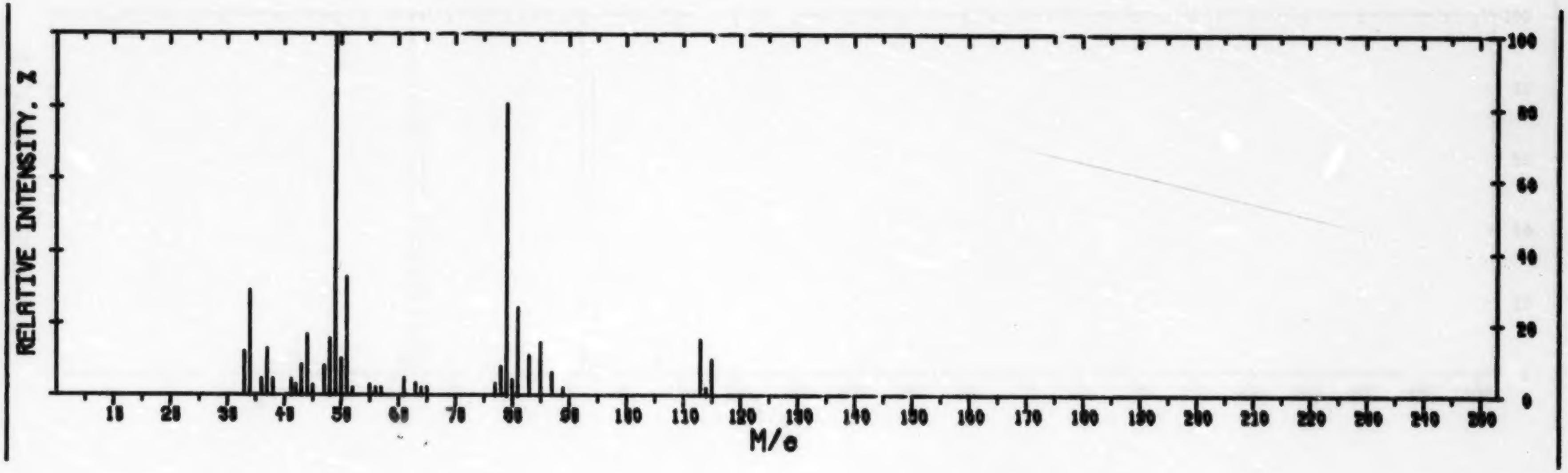

Figure 46. GLC-MS of bis-(chloromethyl)ether

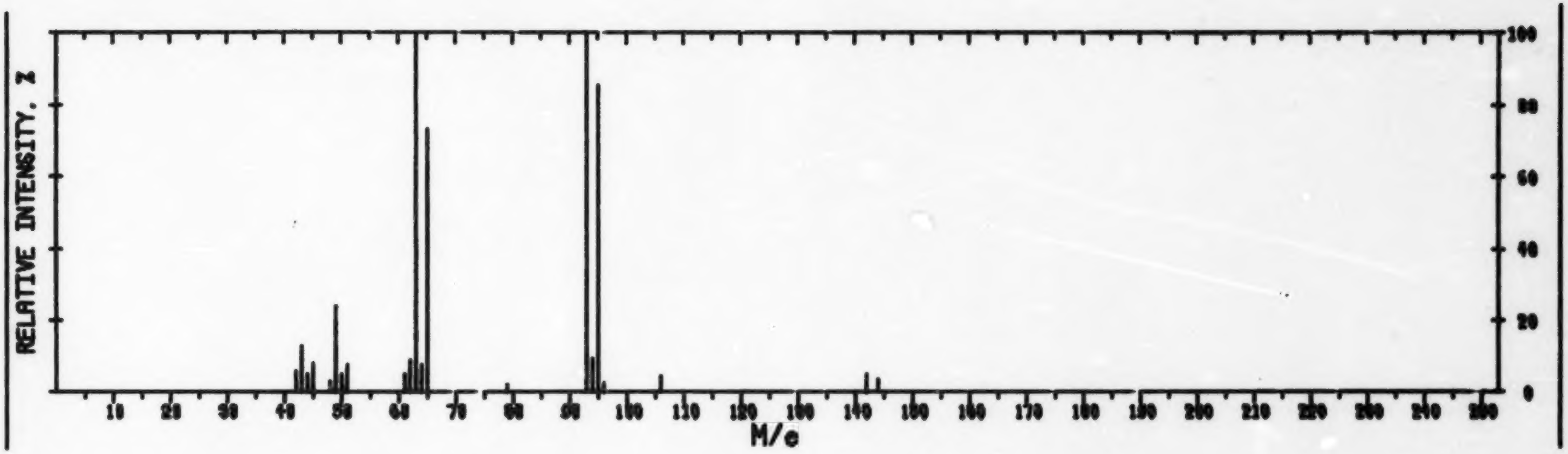

Figure 47. GLC-MS of bis-(2-chloroethyl)ether.

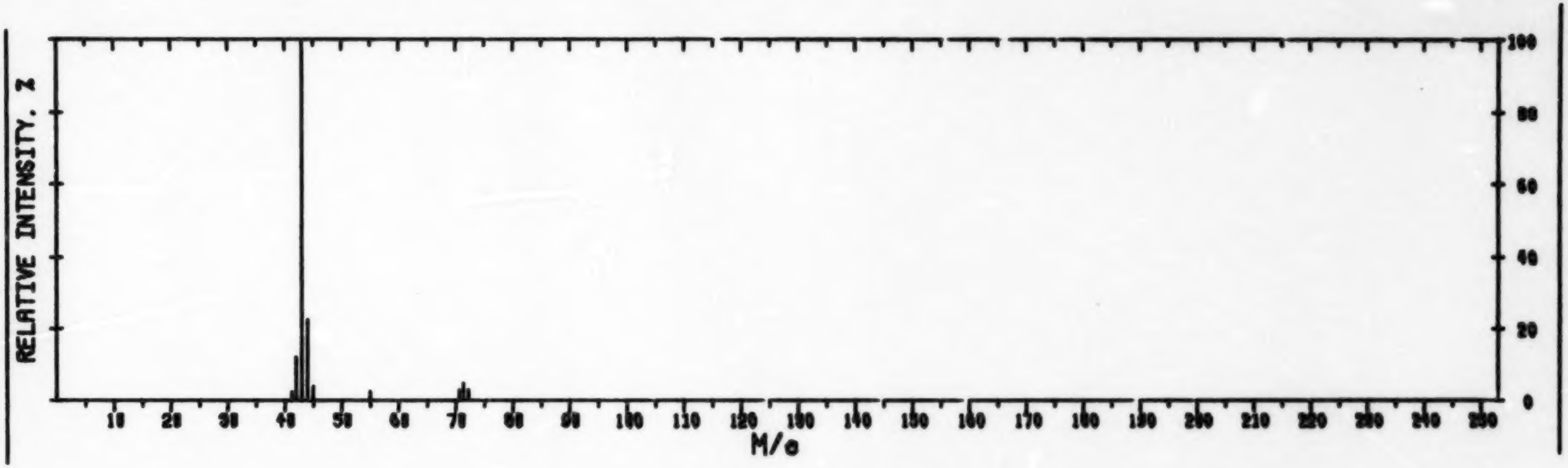

Figure 48. GLC-MS of β-propiolactone.

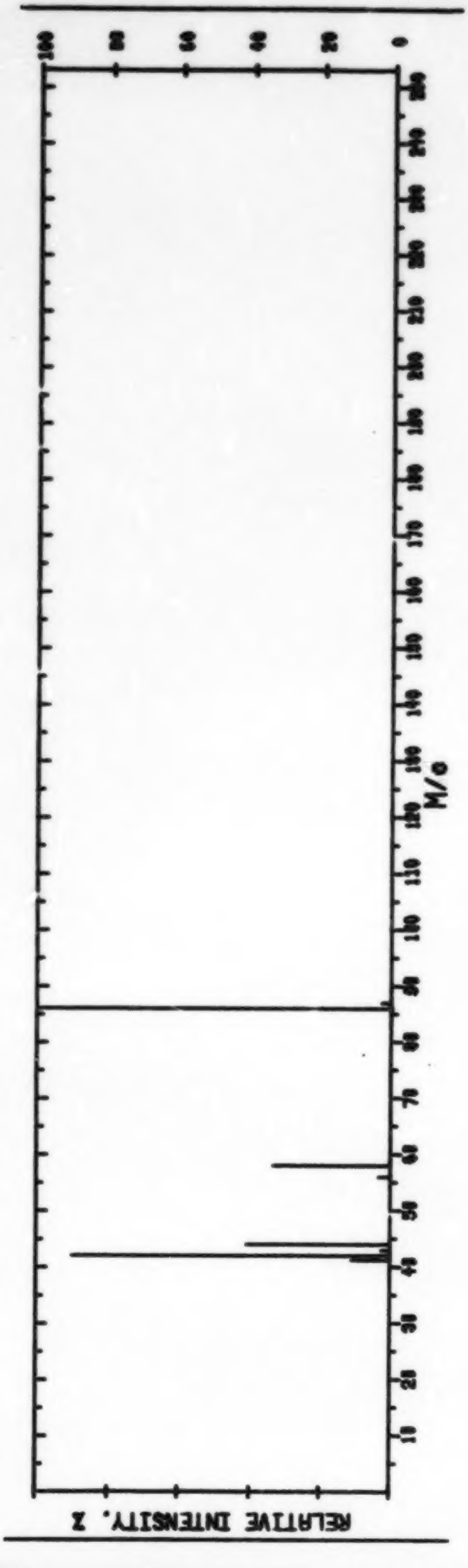

Figure 49. GLC-MS of vinylene carbonate.

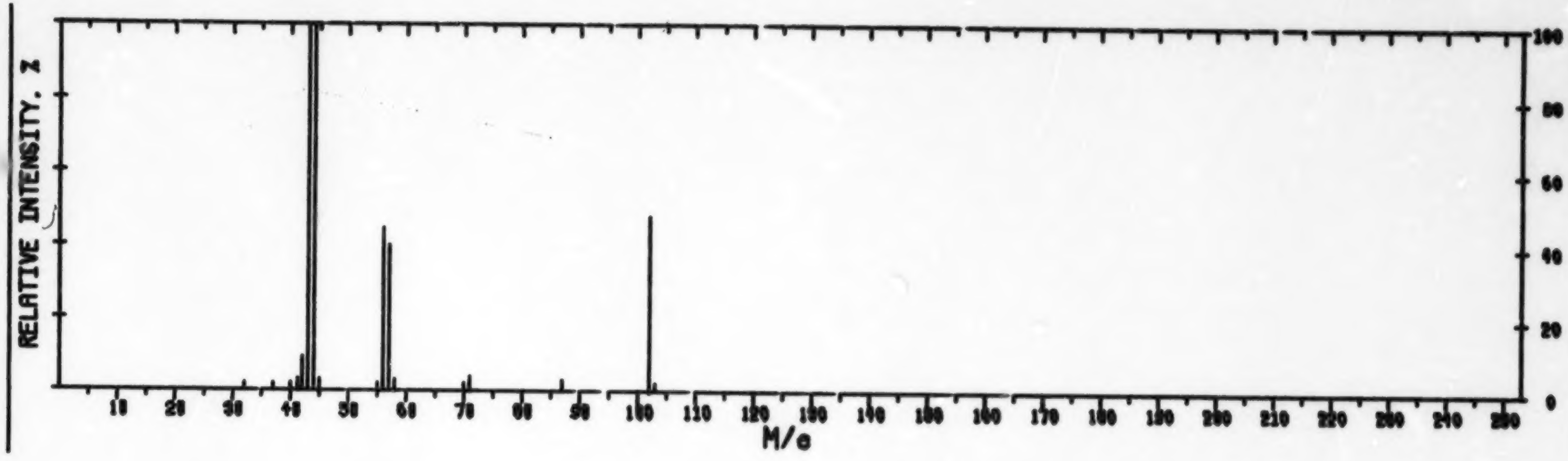

Figure 50. GLC-MS of N-diethylnitrosamine.

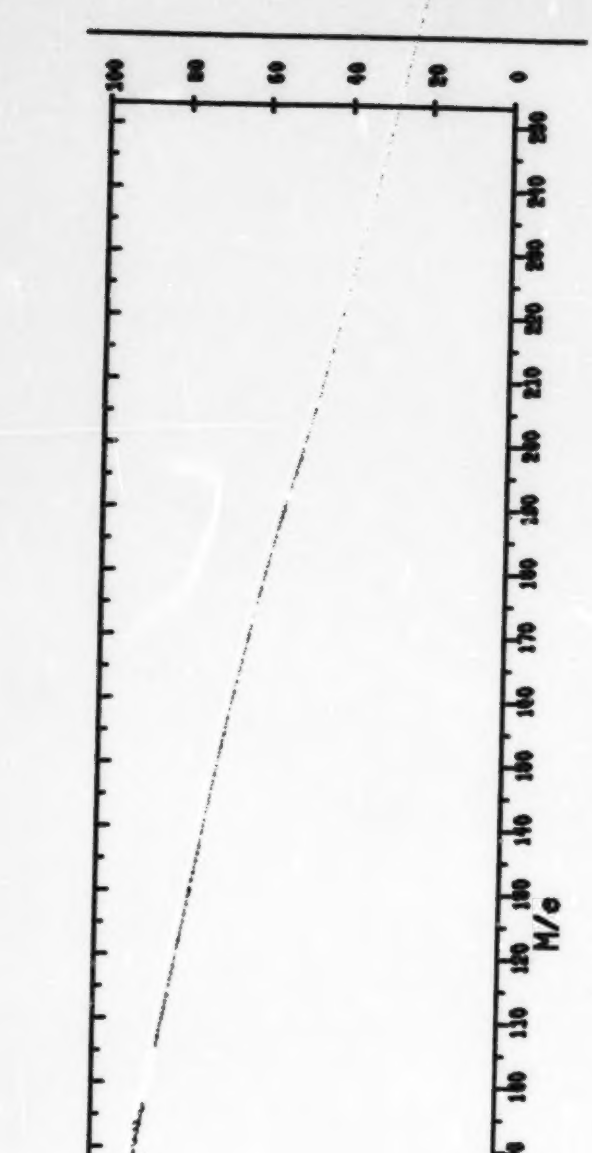

Figure 51. GLC-MS of nitromethane

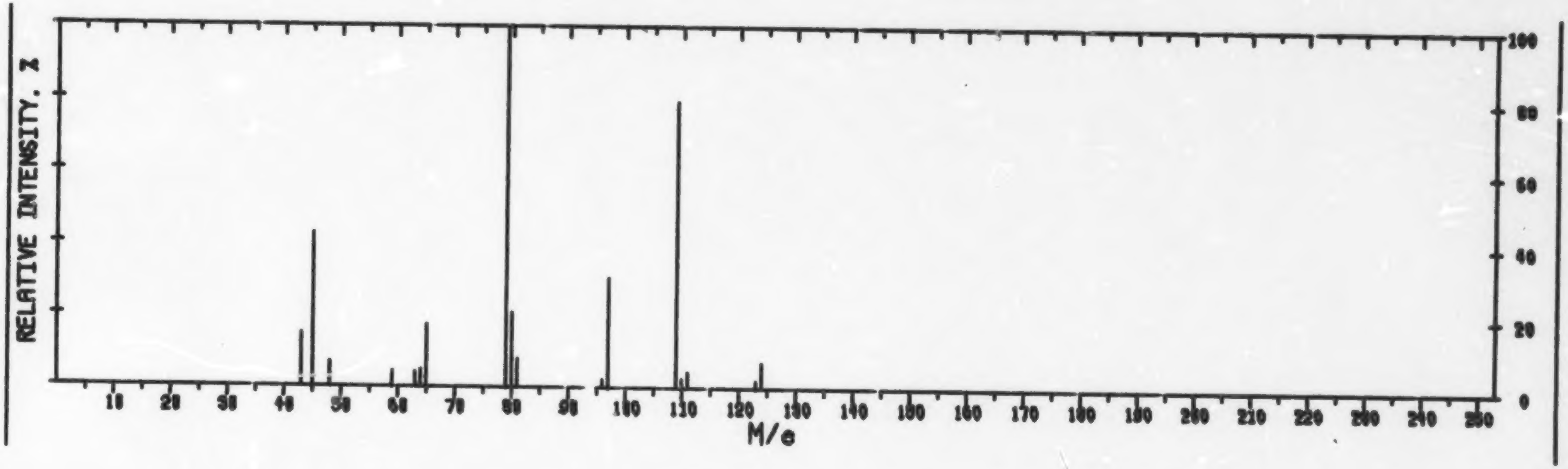

Figure 52. GLC-MS of ethylmethanesulfonate.

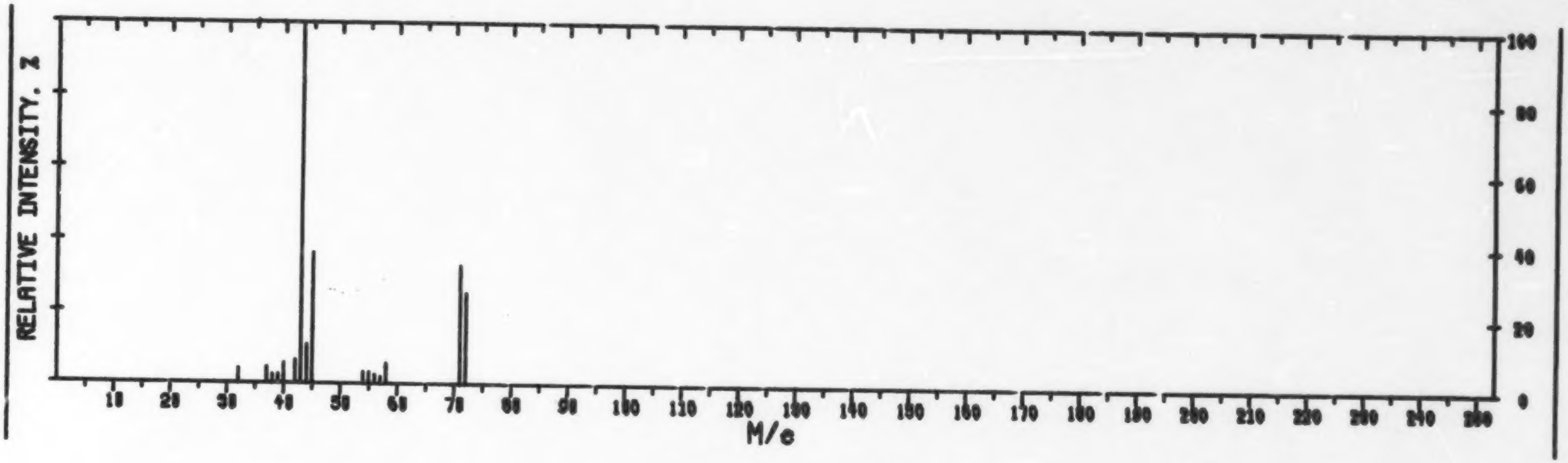

Figure 53. GLC-MS of glycidaldehyde.

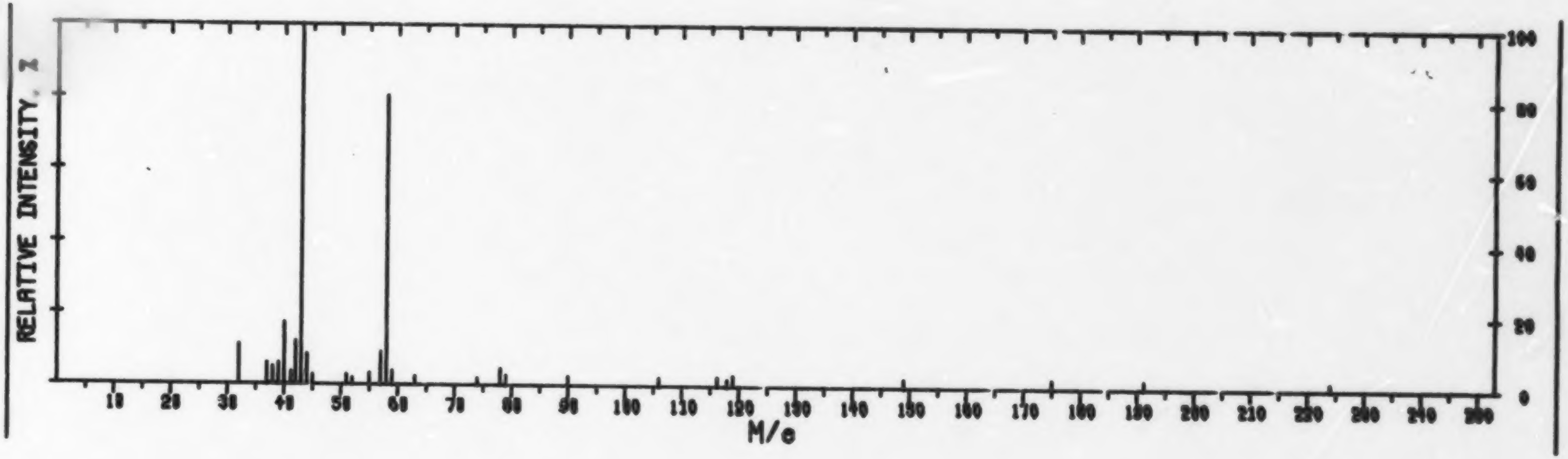

Figure 54. GLC-MS of propylene oxide.

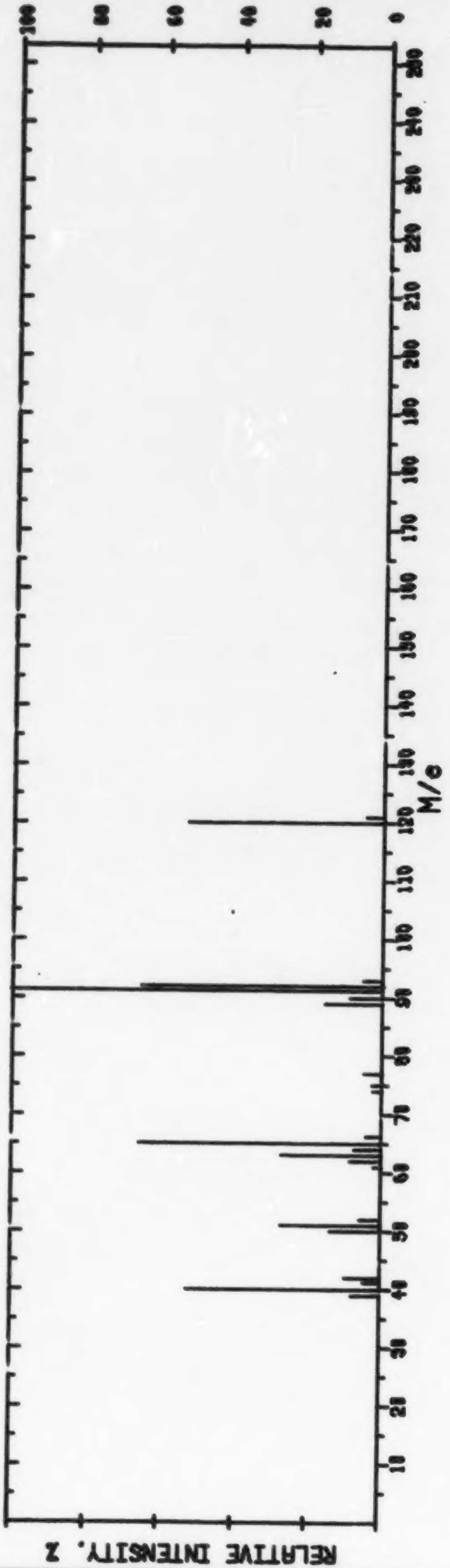

Figure 55. GLC-MS of styrene oxide.

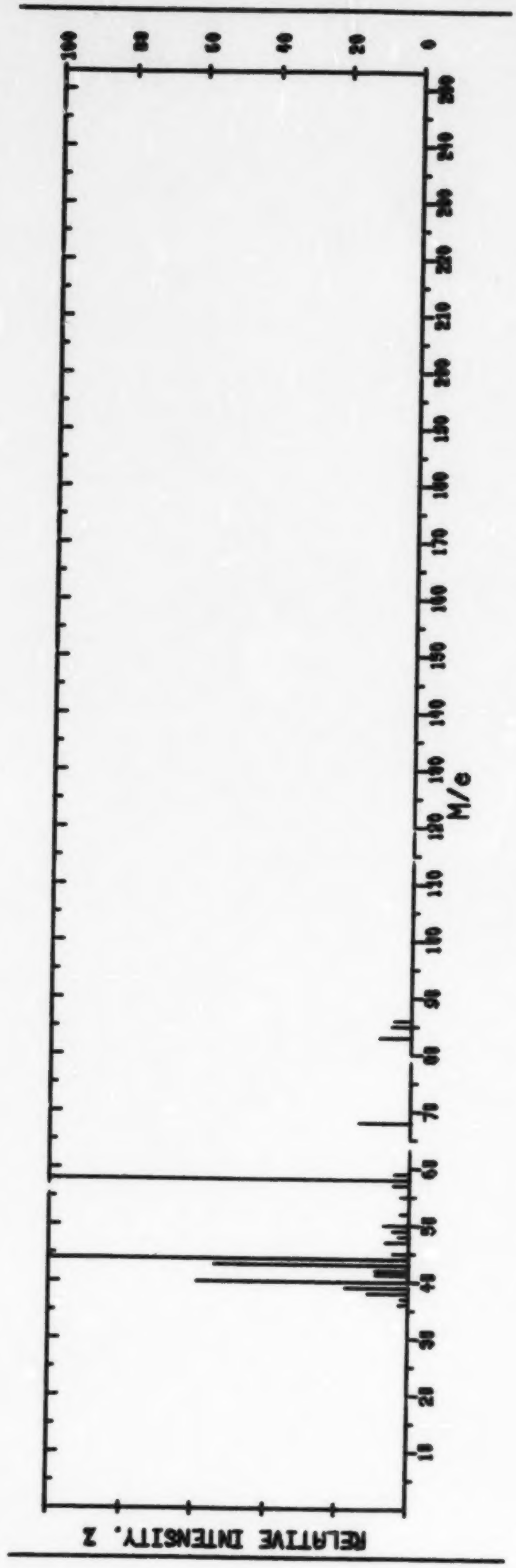

Figure 56. GLC-MS of butadiene diepoxide.

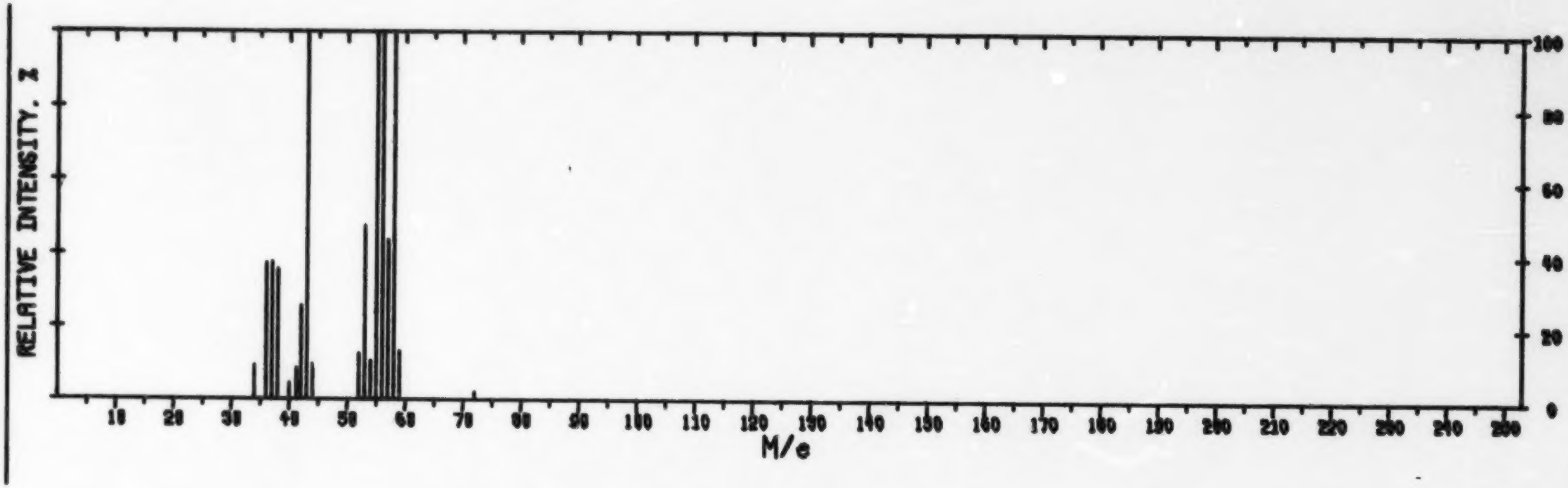

Figure 57. GLC-MS of acrolein.

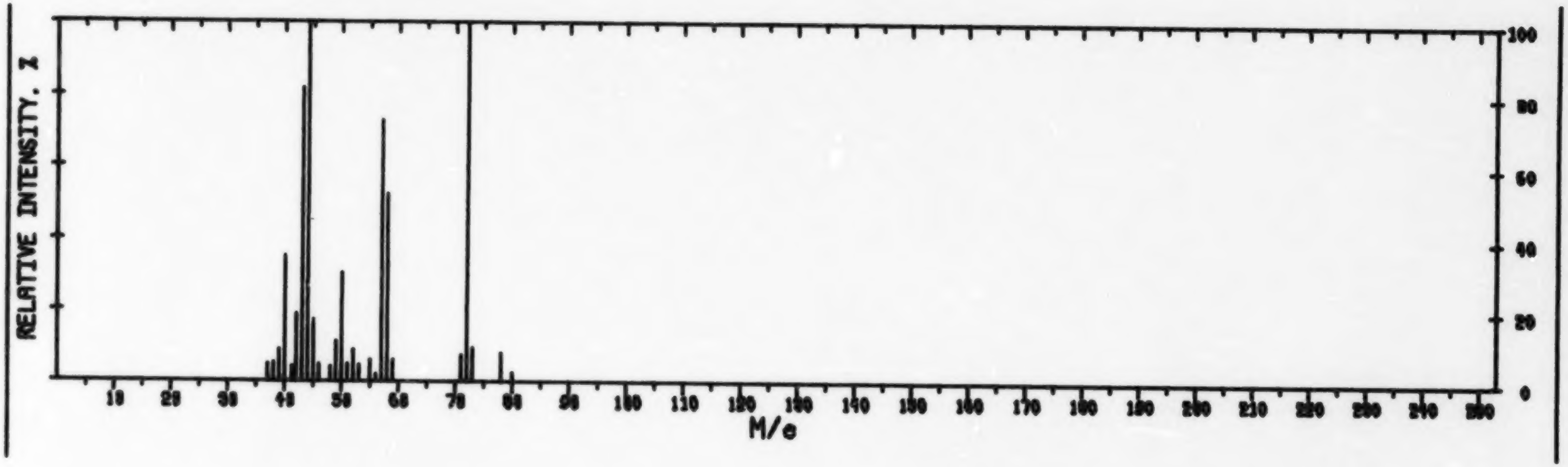

Figure 58. GLC-MS of methyl ethyl ketone.

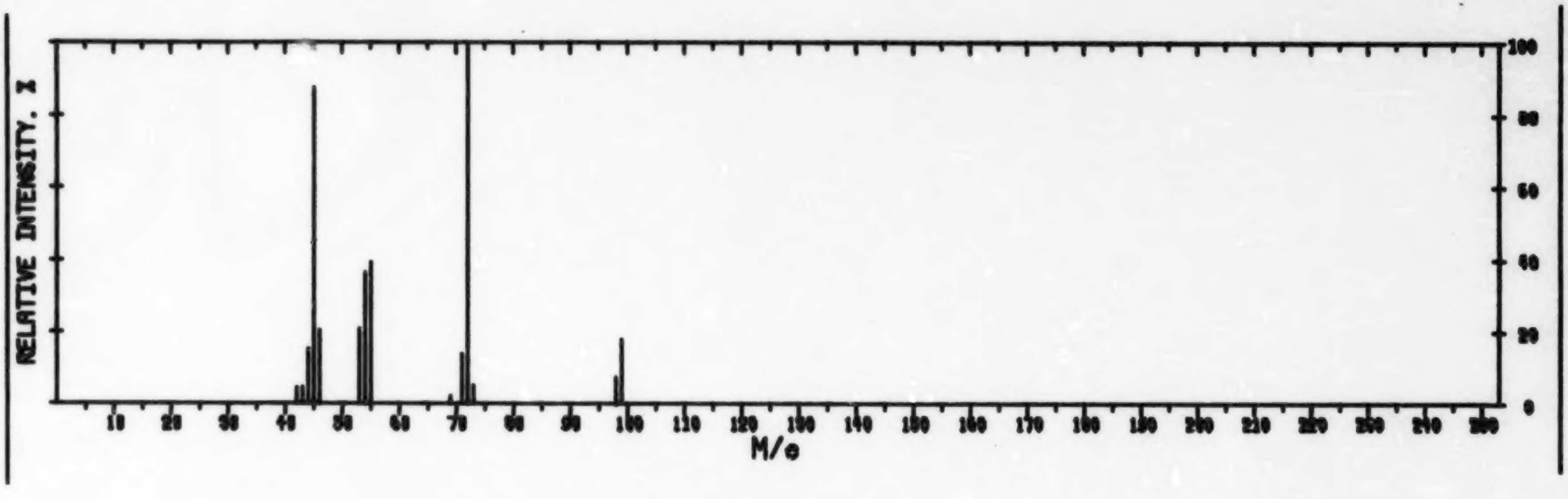

Figure 59. Mass spectrum of maleic anhydride.

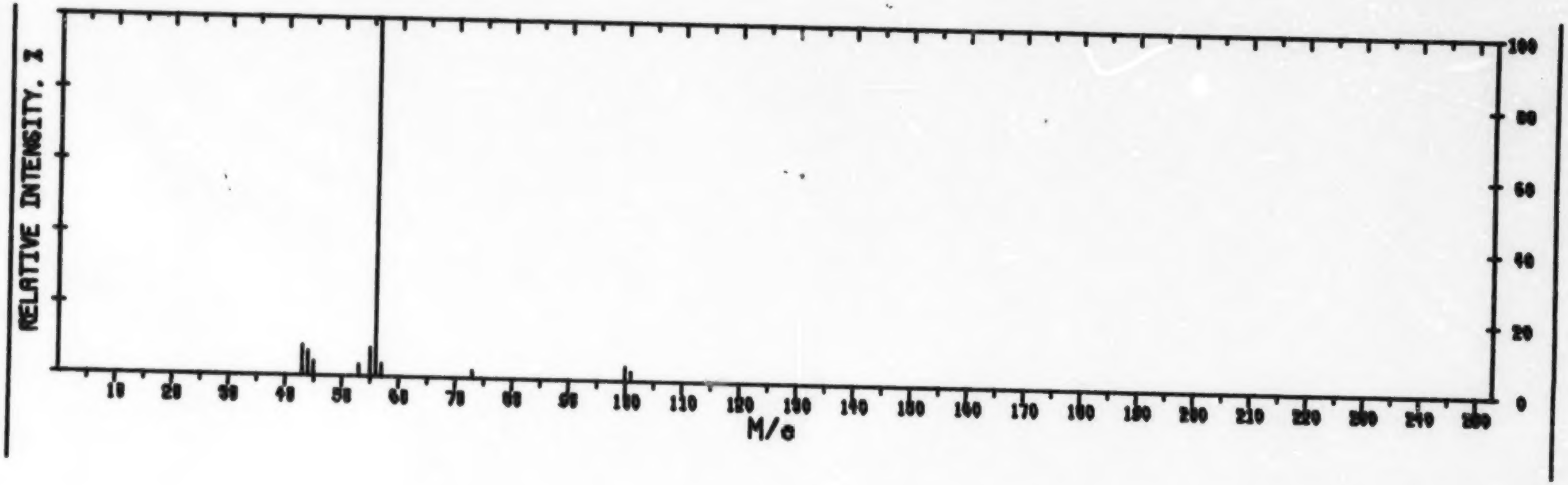

Figure 60. Mass spectrum of succinic anhydride.

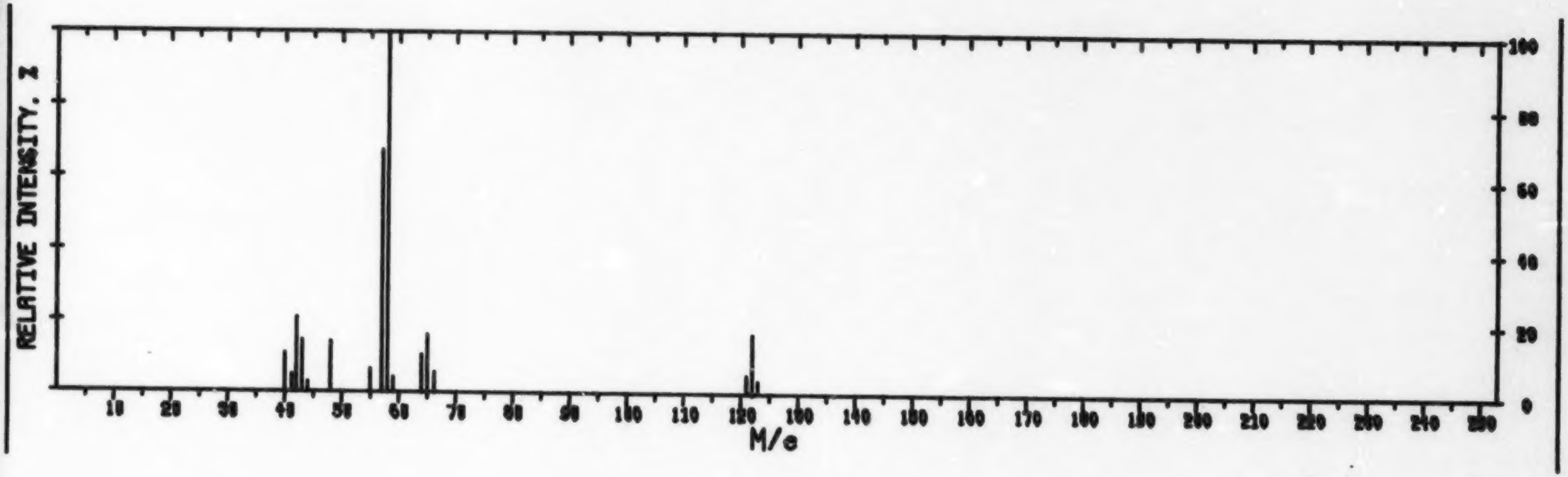

Figure 61. Mass spectrum of 1,3 propane sultone.

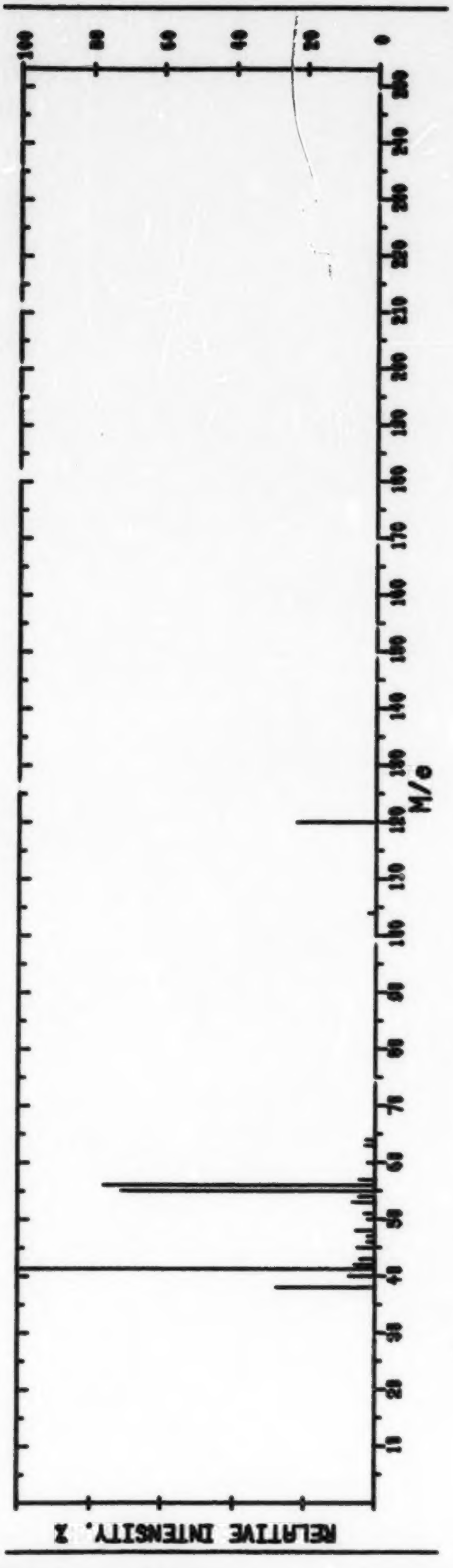

Figure 62. GLC-MS of tetramethylene sulfolane.

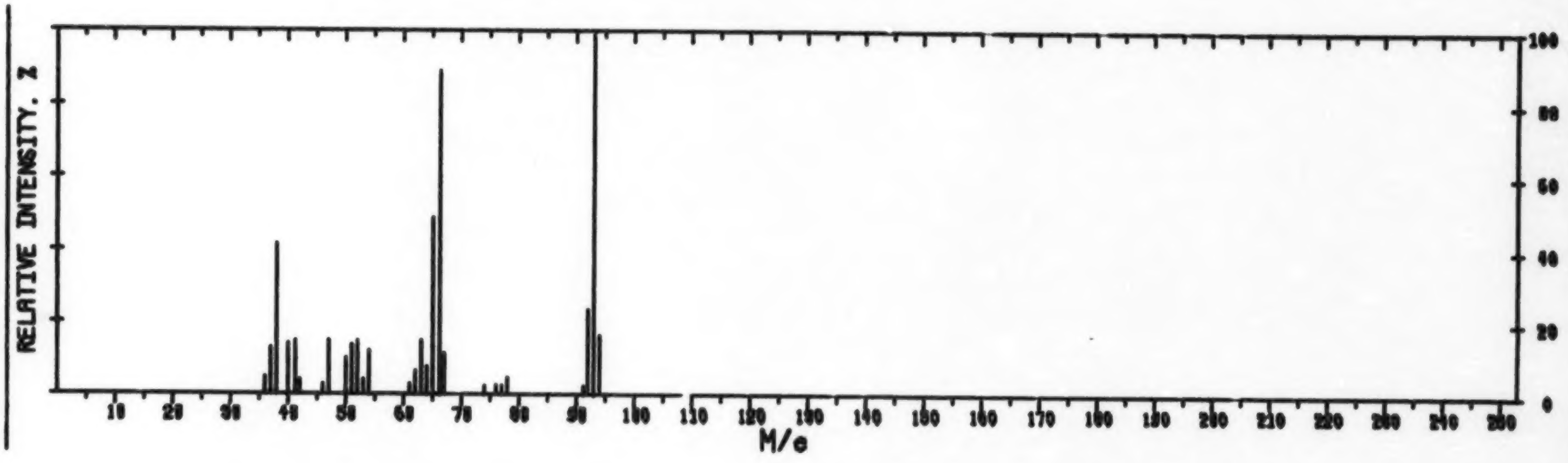

Figure 63. GLC-MS of aniline.